ICOM COMMITTEE FOR CONSERVATION

8th Triennial Meeting
Sydney, Australia
6–11 September, 1987

Preprints Volume III

COMITÉ DE L'ICOM POUR LA CONSERVATION

A Note on the Cover

The bark painting, ochre on stringy-bark, is by Bargudubu of the Gunwinggu tribe, Western Arnhemland. The rainbow serpent, Ngalyod, is the most important creator spirit in the mythology of Arnhemland Aborigines. It is believed to have many different manifestations and is known by various names. The Gunwinggu people believe Ngalyod is the mother creator from whom they are descended. She is particularly associated with women's ceremonies, the conception of children, the cycle of seasons, and the regeneration of all living things. If tribal laws are broken, Ngalyod takes revenge by sending droughts, cyclones, and floods.

Photography by Jennifer Steele. Reproduced by permission of the Aboriginal Artists Agency, Sydney.

The hornbill wood carving (back cover) was made by the Abelam people of Papua New Guinea. The hornbill is an important totemic figure in the Abelam ceremonies and is normally attached to the façade of men's spirit houses used for secret initiation rituals.

Photography by the Australian Museum. Reproduced by permission of the Australian Museum.

Note explicative sur l'illustration en couverture

Le tableau peint sur écorce d'eucalyptus, ocre sur écorce filandreuse, est l'oeuvre de Bargudubu de la tribu Gunwinggu, Terre d'Arnhem de l'ouest. Le serpent arc-en-ciel, Ngalyod, est l'esprit créateur le plus important dans la mythologie des Aborigènes de Terre d'Arnhem. Il passe pour se manifester sous de multiples formes et est connu sous divers noms. Le peuple Gunwinggu croit que Ngalyod est la mère créatrice dont ils descendent. On l'associe surtout aux cérémonies chez les femmes, à la conception des enfants, au cycle des saisons, et à la régénération de tout ce qui vit. Si les lois tribales se trouvent enfreintes, Ngalyod prend sa revanche en produisant séche-resse, cyclones, et inondations.

Photographie: Jennifer Steele. Reproduction faite avec l'autorisation de l'Aboriginal Artists Agency de Sydney.

La sculpture sur bois du calao (en dos de couverture) a été exécutée par le peuple Abelam de Papouasie Nouvelle-Guinée. Le calao se veut une representation totémique importante dans les célébrations rituelles des Abelams. Elle est généralement fixée à la façade des maisons des esprits, réservées aux rites secrets d'initiation chez les hommes.

Photographie: The Australian Museum. Reproduction faite avec l'autorisation de l'Australian Museum.

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Working Group 17

Lighting and Climate Control

Eclairage et contrôle du climat

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TRIENNIAL OVERVIEW

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PROGRAMME 1985-1987

Climate:

1. Collect information on producers of instruments measuring, registering, modifying climate and distribute it with possible comments from users.

2. Make a study (of at least one year) of climate in a showcase, using different kinds of buffer agents.

3. Collect information on national climate standards in museums (if any).

Light:

1. Collect information on producers of measuring instruments (for visible and invisible radiation).

2. Collect information on special light sources and protective film, varnish, etc. Distribute this information with comments.

3. Collect information on lighting standards for museums.

SUMMARY

Not all of the points in the Copenhagen programme were dealt with, particularly those concerning lighting.

However, for the section on climate, many colleagues studied how active or passive methods were used, with greater or lesser success, to modify relative humidity in showcases as well as in rooms. The increase of interest in using saturated salt solutions should be underlined as well as the tendency to question the generally-advised standards.

Finally, quite a few articles were jointly taken up by curators, architects and conservators/restorers, which should encourage an even more active collaboration between these three branches of the profession to better ensure satisfactory conservation of the collections.

POUR UNE NOUVELLE APPROCHE DES NORMES CLIMATIQUES DANS LES MUSEES

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ABSTRACT

Climatic standards for museums have been established on the basis of empirical data gathered only in England or on scientific data referring mainly to new materials, which are hardly comparable to museum objects. A brief analysis of how such standards are defined and a comparison of the figure proposed in the literature point up contradictions and a lack of scientific accuracy. Meanwhile, until research has developed further, another approach to standards is proposed. It is based on the fact that the t° is of minor importance and on the principle that the "ideal" RH is that to which the object has become accustomed in the past. As a result, it is essential to know the object's curriculum vitae in order to determine the proper RH.

RESUME

Les normes climatiques pour les musées ont été définies sur des données empiriques vérifiées en Angleterre seulement et sur des données scientifiques concernant surtout des matériaux neufs, peu comparables aux objets de musées. Une brève analyse de la façon dont les normes sont définies et une comparaison des chiffres proposés par la littérature mettent en évidence des contradictions et un manque de rigueur scientifique. En attendant que les recherches se développent, une autre approche des normes est proposée. Elle est basée sur le fait que la t° a peu d'importance et sur le principe que l'HR "idéale" est celle à laquelle l'objet s'est accoutumé dans son passé. Par conséquent, pour la déterminer, il est essentiel de connaître le curriculum vitae de l'objet.

Introduction

A l'heure où il n'est plus nécessaire de démontrer que le contrôle de l'environnement climatique est une condition primordiale à la conservation des objets muséaux, il est peut-être temps de faire le point sur les modalités de ce contrôle, notamment sur les normes que la littérature continue de proposer dans ce domaine.

Selon les sources, les normes climatiques généralement conseillées sont, pour l'Humidité Relative (HR), autour de 55%, et pour la température (t°), entre 16 et 24°C. Si l'on considère maintenant la réalité, on constate que les climats européens ne sont pas très éloignés de celui défini par ces chiffres. Par contre, pour la majeure partie des autres pays du globe, les moyennes annuelles sont bien plus élevées ou bien plus basses que les normes conseillées. Et pourtant, des collections de toute nature s'y sont parfaitement conservées. On peut citer, par exemple, la collection de 500 statues d'ivoire du Musée Historique National de Rio de Janeiro, qui reste en excellent état à un taux d'HR de 80%; ou encore, le mobilier funéraire très varié découvert dans la tombe de Toutankhamon, qui survécut pendant 3750 ans, sans dommages majeurs, à une HR de 28%!

Comment expliquer ce décalage entre la théorie diffusée aux quatre coins du monde et la réalité?

Origine des normes

Les normes concernant les conditions climatiques dans les musées ont été d'abord déterminées à partir de l'expérience acquise au cours de la dernière guerre mondiale(1). De cette époque, une anecdote est rapportée par H.J. Plenderleith(2), reprise ensuite par de nombreux auteurs: un certain nombre de collections, notamment de peintures de chevalet, furent déposées dans des abris où l'air était stabilisé à 58% d'HR. On constata alors que, pendant cinq ans, les interventions du restaurateur s'espacèrent progressivement, ce qui ne fut pas le cas, ni avant la guerre, ni après, lorsque les oeuvres retournèrent dans les salles d'exposition.

De telles expériences furent capitales, car elles illustrèrent l'action de l'environnement sur les objets de musées et l'importance de stabiliser le climat autour d'eux pour réduire la détérioration. Mais il ne faut pas oublier que ces expériences ont été menées en Europe, particulièrement en Angleterre, et qu'en conséquence, on ne peut en extrapoler, tel quel, l'enseignement à tous les cas. R.D. Buck remarquait(3) par exemple, qu'une HR de 58%, telle qu'elle était conseillée par H.J. Plenderleith, était très difficilement applicable dans la plupart des climats nord-américains.

Outre ces bases empiriques, les normes ont été aussi définies à partir d'études scientifiques sur le comportement des matériaux. La plupart de ces études furent menées dans le domaine militaire ou industriel(4) et non dans celui de la conservation. Par conséquent, les normes qu'elles recommandent sont adaptées à des matériaux neufs et sont établies selon des critères qui ne correspondent peut-être pas au cas des objets de musée. On peut donc poser la question: ces normes sont-elles directement applicables à des matériaux qui ont subi des processus de vieillissement ou qui sont détériorés? Malheureusement trop peu de recherches ont été faites dans ce sens et les difficultés posées par leur réalisation ne justifient pas complètement cette lacune. A notre connaissance, il existe une étude, de R.D. Buck, qui démontre que l'âge du bois, lorsque celui-ci est en bon état, ne modifie pas sensiblement ses propriétés hygroscopiques (5). A part celle-ci, les affirmations concernant la relation entre le vieillissement des matériaux et l'HR ne sont jamais scientifiquement prouvées.

Ces brèves considérations historiques et scientifiques n'ont pour but que d'attirer l'attention sur la relativité des normes proposées: des notions empiriques recueillies dans un seul pays du monde et des expériences sur des matériaux neufs, selon des critères propres à d'autres domaines que le nôtre. Il serait utile d'étudier un ré-ajustement de ces normes en fonction des caratéristiques propres aux objets de musées, notamment leur provenance.

Lorsque l'on examine la façon dont les normes sont présentées, d'autres éléments viennent prouver cette nécessité.

Présentation et détermination des normes

En général, les normes concernent l'HR et la t°. Or, même si certains auteurs expliquent le rôle mineur de la t°, d'autres restent très confus à ce sujet. Ce n'est pas le cas de R.H. Lafontaine et P.A. Wood qui ont comparé les variations dimensionnelles de l'ivoire en fonction de la t° et de l'HR[6]: quand l'HR est fixe à 50% et que la t° varie de 5° à 35°C, les variations dimensionnelles radiales de l'ivoire sont de 0,1%. A l'opposé, quand la t° est fixe à 20°C et que l'HR varie de 20 à 80%, les variations dimensionnelles radiales de l'ivoire sont de 4%, soit 40 fois plus! On peut prévoir des résultats analogues pour les autres matériaux hygroscopiques, même s'il serait nécessaire d'en avoir la confirmation par d'autres études comme celle citée ci-dessus. Quant aux matériaux inorganiques, à l'exception de cas très particuliers comme certaines collections minéralogiques[7], les variations de t° existant normalement dans les musées ne posent pas de problèmes majeurs.

Les normes peuvent être présentées de deux façons:
- soit sous forme d'une fourchette de valeurs, définies par des extrêmes,
- soit sous forme d'une valeur fixe, tempérée d'une marge de tolérance.

Dans le premier cas, les "limites de sécurité" sont déterminées à partir de "l'étude des phénomènes qui accompagnent la dessication des matériaux hygroscopiques" pour la limite inférieure, et par "la découverte des conditions dans lesquelles se développent les microorganismes", pour la limite supérieure[8].

Les normes varient selon les auteurs: entre 40 et 50% pour la limite inférieure, entre 65 et 70% pour la limite supérieure. En ce qui concerne la limite inférieure, malgré la variété des chiffres donnés, tirés directement d'autres domaines ou ajustés de façon totalement arbitraires, on ne peut remettre en question la réalité qu'ils représentent: lorsque l'HR baisse, tout matériau hygroscopique perd proportionnellement la vapeur d'eau qu'il contient, se déssèche, se contracte, devient fragile et cassant, dangereux à manipuler et peut se détériorer.

Mais ce qui est important, comme l'explique K.J. Macleod [9], en prenant l'exemple du bois, c'est l'équilibre entre la teneur en vapeur d'eau (VE) du matériau et l'HR environnante, particulièrement au moment où l'objet a été fabriqué. C'est idéalement cette valeur de l'HR qui serait la plus adaptée à la conservation de l'objet, même si elle est en dehors des marges généralement proposées. Si on considère la courbe de teneur en VE à l'équilibre du bois, par exemple, on peut constater qu'entre 40 et 60%, les échanges de VE entre le matériau et l'air ambiant sont moindres. Ce qui signifie que les variations dimensionnelles du bois sont moins importantes lorsque l'HR varie entre 40 et 60% que lorsque qu'elle varie entre 20 et 40% ou entre 60 et 80% par exemple. Cette constatation pourrait justifier dans une certaine mesure la marge 40-60% conseillée par les normes.

Mais imaginons par exemple le cas d'objets en bois produits dans une région désertique où la moyenne annuelle d'HR est autour de 30%. Il est sûr qu'au cours du temps, un certain nombre de ces objets, peut-être même la majeure partie se seront détruits en raison des conditions adverses. Une sorte de sélection naturelle a eu lieu. De cette production, les objets qui nous sont parvenus, c'est-à-dire ceux qui ont survécu, se sont désormais habitués à ces conditions de sécheresse. Vouloir modifier ces conditions pour entrer dans la "normalité" pourrait leur être fatal!

On peut raisonner de la même façon pour des objets provenant de zones humides et penser qu'ils seront mieux préservés dans un climat humide. Quant aux problèmes de croissance de microorganismes qui permettent de fixer une limite supérieure de l'HR, on peut aussi exprimer quelques réserves: d'une part, parce que cela dépend beaucoup du matériau. En effet, on a pu démontré que ce n'est pas tant l'HR qui est importante, mais la teneur en VE du matériau[10]. Ce qui signifie que plus celui-ci est hygroscopique, plus il est sensible aux microorganismes. Par exemple, certains cuirs, en raison de méthodes de tannage qui introduisent des sels hygroscopiques dans le matériau, peuvent se couvrir de moisissures à des taux d'HR bien inférieurs de celui conseillé par les normes. D'autre part, si on respecte tous les enseignements des biologistes, une HR élevée est une condition nécessaire à la croissance des microorganismes, mais pas suffisante. La t°,

la ventilation de l'air et l'obscurité jouent aussi un rôle de première importance.

Si on considère maintenant les normes fixes et les marges de tolérance proposées, il n'y a que l'embarras du choix: "plus ou moins 2%", "3%", "5%", "6%", "jamais plus de 7%". Sur ce point encore, chacun a son idée, quelquefois, il faut le dire, bien loin des contraintes de la réalité: Comment contrôler en effet, ces variations de plus ou moins 1%, lorsque les fabricants de thermo-hygrographes dénoncent dans les notices d'emploi des instruments, des marges d'erreur de l'ordre de "plus ou moins 4%"!!!

Tableaux de recommandations

De nombreux auteurs affectionnent les tableaux de recommandations, les proposant, selon les goûts, en fonction des matériaux ou en fonction des types d'objets. Les contradictions que l'on peut relever d'un tableau à l'autre et les justifications plus ou moins confuses qui les accompagnent laissent vraiment pensif quant au crédit qu'on peut leur accorder.

Ainsi, il peut être très amusant de les lire et de les comparer. On peut voir par exemple, les laques japonaises et coréennes "catégoriquement" séparées de la laque chinoise [11], ou bien l'os et l'ivoire anatomiques requérant une HR différente de l'os et l'ivoire sculptés (40-60% pour les premiers contre 30-60% pour les seconds!) [12]...

Quelquefois, des spécifications sont données pour les matériaux détériorés. Pour les céramiques, par exemple, on peut trouver de "20-60% selon les incrustations de sels" ou "aussi sec que possible lorsqu'elles sont archéologiques". Voilà deux recommandations difficiles ou dangereuses à appliquer! Quant aux métaux, on trouve selon les sources, "inférieur à 30%" ou entre "15 et 40%", de "20 à 40%", de "20 à 30%"... Chacun propose ses normes, souvent peu discutées...et donc discutables. Même un des co-auteurs de cet article n'a pas su résister à la tentation de faire son petit tableau de recommandations! [13]

En fait le problème majeur et récurrent dans le domaine de la conservation est la volonté d'adopter une démarche scientifique sans en avoir pourtant la rigueur. Il n'est pas question de critiquer ni de mépriser ces tentatives de "réglementation" du climat par ailleurs louables puisqu'elles ont voulu, à un moment donné, remédier à une situation d'ignorance ou d'indifférence et provoquer une prise de conscience. D'ailleurs, de nombreux auteurs tempèrent les chiffres qu'ils conseillent en expliquant toutes les exceptions à la règle. On peut, à ce propos, citer l'excellent chapitre de G. Thomson, dans l'ouvrage qui vient d'être réédité "The Museum Environment"[14]. L'auteur y mentionne aussi les difficultés posées par l'étude de la relation des phénomènes de détérioration des objets muséaux en fonction de l'HR. Effectivement, en consultant la littérature, on peut remarquer que lorsqu'il s'agit de détériorations chimiques ou biologiques, des études rigoureuses existent. On peut citer, à titre d'exemple, les recherches de R.H. Brill sur les verres instables[15]. Par contre, en ce qui concerne les phénomènes de détérioration mécanique, les hypothèses de travail sont très difficiles à élaborer et les travaux manquent.

Une alternative aux normes

En attendant que se développe la recherche dans ce domaine, il est très important d'inviter les conservateurs à une lecture critique des normes diffusées par la littérature et d'aborder sous une autre forme le problème de détermination du meilleur environnement pour les objets de musée.

Une possibilité serait de considérer les critères caractéristiques de ces objets:

- le matériau
- les techniques de fabrication
- le passé de l'objet
- les altérations subies

\- Le matériau:
Il s'agit bien sûr du critère de base, puisque lorsque le matériau est organique, il est directement sensible à l'HR. Par contre, pour les matériaux inorganiques, l'action combinée d'au moins un autre facteur détermine la détérioration. Ce facteur peut être dans l'environnement: oxygène, agents polluants...ou dans l'objet lui-même: vice inhérent, présence de sels... Ce qui nous conduit à envisager avec la même importance les critères suivants:

- Les techniques de fabrication ou de construction:
On peut considérer ce critère d'un point de vue mécanique: un objet composite est plus sensible qu'un objet composé d'un seul matériau. Pour le cas particulier des matériaux hygroscopiques, leur épaisseur ou leur volume, l'orientation dans laquelle ils ont été taillés ou fabriqués (s'ils sont anisotropes) peuvent influencer les risques de détérioration dues aux variations d'HR. D'un point de vue chimique, la composition de certains produits, comme certaines qualités de verres, de papiers..., les rend plus sensibles que d'autres à l'action du climat.

- Le passé de l'objet:
Ce critère est primordial, quelque soit le type d'objet. Considérons, par exemple, le cas des matériaux organiques. Un des exercices créés pour les cours de l'ICCROM par R.M. Organ s'intitule "Comment demander à l'objet l'HR à laquelle il était accoutumé". Dans ce texte, l'auteur postule que le contenu en VE de l'objet dépend de son "histoire immédiatement précédente". Par conséquent, en plaçant l'objet dans un volume extrêmement restreint et clos, l'HR de ce milieu se mettra naturellement en équilibre avec le contenu de VE de l'objet, indiquant au bout d'un laps de temps l'HR à laquelle celui-ci était accoutumé. L'idée est intéressante: en effet, maintenir l'objet à l'HR à laquelle il était accoutumé signifie maintenir son contenu de VE d'origine, c'est-à- dire empêcher les variations dimensionnelles qui seraient une cause de détérioration.

- Les altérations chimiques ou physiques subies pendant le passé:
Certains matériaux ont fait l'objet d'études poussées, comme c'est le cas des bronzes archéologiques. Pour d'autres, les connaissances sont limitées et les conséquences de la relation entre ces altérations et l'HR sont difficiles à prévoir et donc à contrôler.

Conclusions

Lorsqu'on veut déterminer le meilleur environnement pour un objet de musée, il est essentiel de tenir compte non seulement du ou des matériaux qui le composent, mais de son curriculum vitae, c'est-à-dire de l'ensemble des événements historiques et climatiques qui l'ont fait parvenir jusqu'à nous. Dans l'état actuel des recherches, l'application aveugle des normes climatiques proposées par la littérature peut avoir des conséquences néfastes. Il est peut-être préférable de décider des conditions climatiques au cas par cas, en essayant de modifier le moins possible la valeur de l'HR que l'étude du passé de l'objet nous permettra de déterminer. Quant à la t°, il faudrait cesser de lui attribuer un rôle majeur, comme cela a toujours été dit, écrit et répété. En fait, affirmer qu'il faut contrôler l'HR et la t°, c'est juste. Mais c'est aussi faux parce que cela donne une même importance aux deux conditions, ce qui n'est pas le cas dans la réalité. Il faudrait dire: contrôler avant tout l'HR et, lorsqu'on en aura le temps, les moyens techniques et financiers, contrôler aussi la t°.

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(4) G.A. Greathouse and C.J. Wessel: "Deterioration of materials", Reinhold Publishing Company, New York, 1954.

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(6) R.H. Lafontaine and P.A. Wood: "The stabilization of ivory against RH fluctuations", Studies in Conservation, 27, 1982, pp. 109-117.

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(12) N. Stolow: "La protection des oeuvres d'art pendant leur transport et leur exposition", Unesco, Paris (Musées et Monuments), 1979, pp. 121-122.

(13) G. de Guichen: "Climat dans les musées, mesure", Fiches Techniques, Iccrom, seconde édition, 1984, p.67.

(14) G. Thomson: "The museum environment", second edition, Butterworth and Co Ltd, 1986, pp. 82-91.

(15) R.H. Brill: "Crizzling - a problem in glass conservation", Conservation in Archaeology and Applied Arts, London, pp. 112-134.

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IS IT WORTH-WHILE RE-LOOKING AT SALT SOLUTIONS AS BUFFERS FOR HUMIDITY CONTROL OF SHOWCASES?

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SUMMARY

The collection in the Viking Ship Museum, Oslo, Norway, comprises mainly organic material. Salt solutions are used as buffers for humidity control inside the showcases. An RH of about 55% would be suitable, and calcium nitrate is therefore used for the salt solutions. The RH in the showcases stays between 48% in the winter and 62% in the summer, while the RH in the exhibition hall, where there is no climatic control, may vary between 25% in the winter and 85% in the summer. The maintenance of the salt solutions amounts to adding water once a year. "Creeping" of the salt over the edges of the container is no problem.

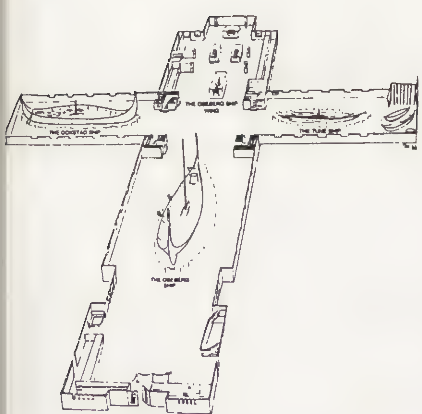

Fig. 1 The Viking Ship Museum. The exhibition hall comprises one big room consisting of four wings, three of which contain the viking ships, and the fourth, the grave finds from the ship burrials.

INTRODUCTION

The Viking Ship Museum in Oslo, Norway, is built in a crosslike form. The first part of the building was finished in 1926, and the last one in 1957. The exhibition hall comprises one big room consisting of four wings, three of which contain the three viking ships. In the fourth wing the grave finds from the ship burials are exhibited in showcases (fig.1). The humidity in the showcases has been controlled by salt solutions since 1957 (1).

This article reviews the experiences from the use of salt solutions for humidity control of showcases in the Viking Ship Museum.

COLLECTION

The Viking Ship Museum comprises the exhibition of three viking ships and a great number of objects which have been found in the ships. All the ships are excavated from burial mounds. The Tune ship was excavated in 1867, the Gokstad ship in 1880, and the Oseberg ship in 1904.

The deceased, that were burried in the ships, had been supplied with all kinds of utensils and equipment which could be needed in a life to come. Particularly well equipped was the Oseberg ship.

The most characteristic finds in the Oseberg ship are the rich content of wooden objects decorated with unique carvings. These objects comprise cart and sledges, sledge shafts, animal head posts, beds etc. Besides the wooden objects there are also a variety of objects for everyday use and objects for decoration in metal, bone, textile, leather and rope.

Ships. While the Gokstad ship was more or less complete at the time of excavation, the Oseberg ship was found in thousands of pieces, broken and twisted by the heavy load of stones and clay in the barrow.

The ship had been burried in blue clay and covered up with turf sods packed thightly together. The ground water level was fairly high. The barrow therefore was more or less airtight and gave good conditions for a natural preservation of the materials of the ship and the grave finds. Despite the mechanical destruction of the objects, the condition of the wood and other materials was for a large part remarkably good at the time of excavation.

The Oseberg ship was restored from thousands of pieces, and the wood was treated with linseed oil and carbolineum. No consolidation treatment was needed.

Fig. 2 A general view of the part of the exhibition hall which contains the showcases with the grave finds.

Conservation of the wooden objects. (1,2) Most of the wooden objects were treated with hot alum, which replaced the water in the wood after drying. At that time this was regarded the best conservation method to avoid deformation of the wood. By this method the shape of the objects are well maintained, while the fine carvings are somewhat blurred.

As alum is a salt which dissolves easily in water, even moderate changes in RH will cause the alum in the surface of the objects t go out and in of solution, resulting in formation of salt crystal on the surface. The alum treated objects has therefore been given a surface coating by a laquer. This seems to provide a satisfactory protection.

The interior of the alum treated wood has become more or less crystalline and is very brittle. The objects can hardly be truste to carry their own weight. However, the alum treated objects in the Viking Ship Museum seem to be in a stable conservation condition as long as the RH is kept fairly steady.

The wooden objects which have the most unique carvings, were stored in water for about 50 years, waiting for a better conservation method. In the middle of the fifties these objects were treated by tertiary butanol in a freeze-drying process.

Some of the objects which were treated with t-butanol, suffered from cracking after they were taken out of the vacuum chamber int the air. However, when stored at an RH of about 55% these cracks are hardly visible. The t-butanol treated objects are in a stable and good conservation state.

Fig. 3 Showcases along the walls.

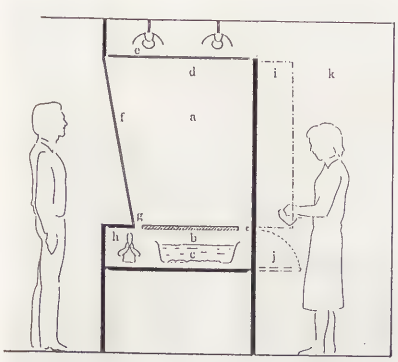

Fig. 4 A cut through one of the showcases along the walls; side view. See text.

SHOWCASES

The showcases in the Viking Ship Museum were built in 1957.

Fig.2 gives a general view of part of the exhibition hall with the showcases. Some of the showcases are placed along the walls of the building, and some are detached in the middle of the room. The showcases along the walls (fig.3) have display windows only in the front, while the detached showcases have display windows in four directions. The showcases are made of wood which is carefully coated with a laquer.

Fig.4 shows schematically how the showcases along the walls are constructed. The exhibits are illuminated by fluorescent tubes (e) above the exhibition space (a). A non-gloss glass (d) forms the ceiling of the showcases. Below the exhibition space there is a separate compartment (b) for containers with salt solutions (c). Small slits (g) in the board between the exhibition space and the salt solution compartments take care of air circulation, which is improved by small electric fans (h). The display window (f) is somewhat tilted (ca. 10°) to avoid or minimize reflexes.

There is access to the exhibition space and the salt solution compartments through separate doors (i,j) at the back of the showcases. A passage (k) between the back of the showcases and the outer walls of the building also prevents a cool wall to be formed in the showcases, where condensation could occur.

The surface area of the salt solutions is about 0.2 m^2 to one cubic meter of air in the showcase.

Also the detached showcases are provided with compartments with salt solutions.

STABILIZATION OF RELATIVE HUMIDITY (RH)

There is no climatic control in the exhibition hall. Both the RH and temperature are therefore influenced by the outdoor conditions, which give a humid season in the summer and a dry season in the winter inside the museum.

During the winter the exhibition hall is heated to about 16-18°C. Although the heating of the building in the winter is pleasant for visitors, this is the crucial point leading to a serious decrease in the indoor RH. During the winter the average outdoor temperature is about -4°C and the RH 80-85% at the location of the Viking Ship Museum (3). When this air enters the museum and is heated to an acceptable indoor temperature, a simultaneous decrease of the RH takes place.

By evaporation of water from the salt solutions inside the showcases the air in this space is humidified in order to compensate for the low RH. The evaporation continues until the salt solutions are in equlibrium with the air in the showcase.

As the organic material is the more sensitive part of the collection, an RH of about 55% is wanted inside the showcases. The humidity control in the showcases is based on saturated solutions of calcium nitrate, ($Ca(NO_3)_2 \cdot 4H_2O$), giving a relative humidity of 56% at 18.5°C (4).

Fig.5 shows the RH and temperature inside the showcases (along the wall) and in the exhibition hall outside the showcases in the "dry season" (winter). The temperature is somewhat higher inside the showcases. This is due to the heating system of the museum, which is installed along the walls not far from the showcases. In the detached showcases, which are far from the heating system, the temperature is approximately that of the exhibition hall. The RH is seen to be much lower in the exhibition hall than inside the showcases (30% and 53%, respectively), where water evaporates from the salt solutions when the air becomes too dry.

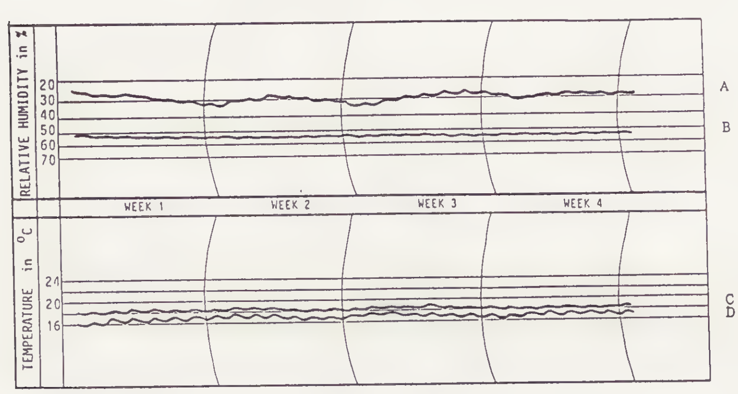

Fig. 5 Recordings from thermohygrographs in the "dry season" (winter). RH in the exhibition hall (curve A) and inside the showcases (curve B). Temperatures inside the showcases (curve C) and in the exhibition hall (curve D).

In the summer the temperature is about the same inside and outside the showcases, influenced by the outdoor temperature. In rainy periods, when the outdoor climate is particularly humid, the RH is higher in the exhibition hall than inside the showcases, where water vapour from the air is absorbed by the salt solutions when the air becomes too humid.

The fact that a showcase is placed inside a museum building will, of course, help to reduce the effect of rapidly changing humidity. Also the wooden framework of the showcases may contribute somewhat to the buffering effect. But owing to a surface coating of the framework by a laquer this effect seems to be minor. The main effect on stabilization of the RH inside the showcases is due to the action of the salt solutions.

Fig.6 gives an outline of the changes of temperature and RH inside the showcases and in the exhibition hall over a year. While RH inside the showcases is seen to fluctuate between 48% in the "dry season" and 62% in the "humid season", the corresponding RH in the exhibition hall fluctuates between 25% and 85%.

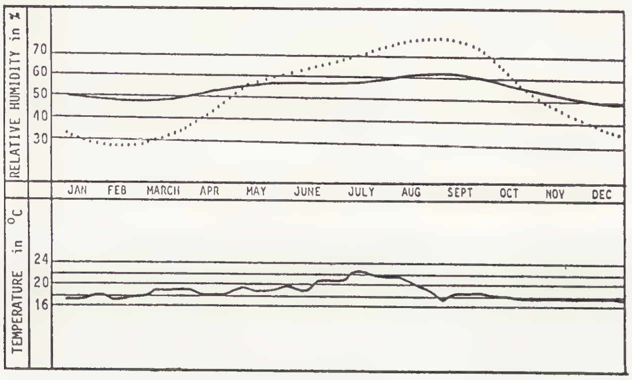

Fig. 6 Average RH and temperatures inside a showcase over a year. The dotted line indicates the average RH in the exhibition hall.

MAINTENANCE

The maintenance of the salt solution system amounts normally to adding water once in the "dry season". The solutions should be stirred when water is added in order to keep a constant concentration.

Containers of PVC are used for the calcium nitrate solutions. There have been no problems with creeping of the salt crystals, i.e. the salt crystals going into and out of solution tend to stick to the walls of the container and gradually move over the edges.

DISCUSSION

It has long been known that saturated solutions of salts in water may be used as buffers for control of relative humidity (RH) in a closed space, i.e. a showcase. Yet, there is little recent litterature on this topic.
On the contrary, the use of silica gel as a buffer for humidity control is frequently discussed.

The fact that silica gel is in the solid state is a great advantage under transport of artifacts. In such cases solutions of salt can, of coures, not be used. For control of RH in showcases in permanent exhibitions it makes little difference whether the buffer is a solid or a solution.
As to the maintenance of the two buffer systems, salt solutions probably involve less work. While the maintenance of a salt solution buffer involves adding more water or increasing the salt concentration, silica gel used for humidification or dehumidification needs to be reconditioned to the wanted RH for about a week or two. The frequency by which maintenance is needed, depends among other things upon the difference in the museum RH and the wanted RH inside the showcases, i.e. the smaller this

difference the longer the system will work. It also depends upon the rate of exchange of air between the inside and the outside of the showcases, which is determined by how tight the showcases are.

One point which is often raised as a problem concerning salt solutions, is their tendency to "creep" over the edges of the container. This seems to be a problem for some salts in containers of certain materials, but it does not take place for other salt/container systems.

As to the cost of the two buffer systems, silica gel is more expensive than salts. However, as neither silica gel nor salt are used up in the process of humidity control the expences may be seen as an investment which will last for years.

CONCLUSION

The stabilization of RH by salt solutions in showcases in the Viking Ship Museum in Oslo is found to work satisfactorily. Based on 30 years of experience it may be concluded that the salt solution system gives a fairly stable RH. Little maintenance is needed in an area where the summer temperatures are tolerable and the winters are cold, and there are no problems with "creeping" of the salt.

As there will always be some exchange of air between the outside and the inside of the showcases, some variations of the RH should be expected during a year. In order to obtain the best possible effect of the salt soultions the exchange of air must be a minimum. The showcases must therefore be as tight as possible.

Although the salt solution system is found to be satisfactory, it may probably be improved in order to obtain a more stable RH with smaller variations inside the showcases. Introduction of more containers with salt solutions and increased surface areas should increase the rate of absorption/evaporation of water molecules. The equilibrium between the salt soultions and the vapour pressure in the air should then adjust more rapidly.
There must always be an excess of solid salt in the container to assure that the solution is saturated.

The effect of increasing the surface area of the salt solutions, i.e. the ratio between the surface area of the salt solutions and the volume of the showcase, will be studied.

In order to obtain the least maintenance the volume of the containers must be large enough to contain enough solution or water for evaporation in the "dry season". In the "humid season", when water is absorbed from the air, the container must be large enough to take up the additional water.

Among the exhibited artifact in the showcases are the unique carved wooden objects from the Viking ship excavations. However, also a number of metal objects, iron and copper alloys, from the excavations are found in the showcases together with the wooden objects. A relative humidity of about 55% was chosen in order to take particular care of the organic material. Inspections of the metal objects show that also these objects survive in a good conservation state without any corrosion.
In theory only water molecules evaporate from the salt solutions as solids ideally does not contribute to the vapour pressure of a solution. In reality this may not be quite true, although the amount of salt leaving the soultion will be minute. One might fear that even minute quantities of salt may catalyse corrosion of metal objects. However, after 30 years, no corrosion has been observed.

Further experiments with other salt systems giving lower relative humidity for storage of sensitive inorganic material (metals), is going on.

Appendix:

THE PRINCIPLES OF CONTROL OF RELATIVE HUMIDITY (RH) BY USE OF SALT SOLUTIONS

A simplified description of the chemical principles of the action of salt solutions used as method for humidity control, may be as follows:

If a container with water is placed in a closed chamber water molecules will evaporate from the surface until the RH in the air above the water is 100%. Expressed in other terms, water exerts a certain vapour pressure at a given temperature.
If a solid compound is dissolved in the water, the vapour pressure above the solution decreases, less water molecules evaporate, and the RH will decrease. The lowering of the RH is dependent on the amount of the compound, or rather the number of particles, which are dissolved in the water.
Every water soluble compound has, at a given temperature a specific solubility; ex. the solubility of NaCl is 35.7 g/100 g water at 0° C, 39.1 g/100 g at 100°C. This corresponds to a saturated solution. If more salt is added, it will not dissolve, but the crystals will gather at the bottom of the solution. The undissolved crytals show that the solution is saturated.
If air of low humidity is introduced into the chamber above the solution, more water molecules will evaporate from the solution until the water vapour and the RH which is characteristic for that particular solution, is obtained. Ideally, a solid compound which is dissolved in water does not contribute to the total vapour pressure above the solution.

If air of high humidity is introduced into the chamber, the solution will absorb water molecules from the air until the characteristic vapour pressure and RH for the solution is obtained.

As water molecules evaporate or are absorbed the volum of the solution will lose or gain, respectively, some little portion of its volum. When water is absorbed by to the solution it will dissolve more of the solid compound, i.e. some of the excess crystals go into solution. Vice versa, when the solution loses water, some of the crystals precipitate in order to maintain the constant concentration, corresponding to saturation.

How fast the RH will adjust when the sytem is disturbed by introducing dry or humid air from the outside, will depend among other things upon the surface area of the solution where the water molecules evaporate or are absorbed, the temperature, and the type of salt used.

NOTES

1. A.M. Rosenqvist, Studies in Conservation, Vol. IV, No. 2 (1959) p. 62.

2. E.E. Astrup, ICOMOS Bulletin, in press.

3. Reports from The Norwegian Meteorological Institute.

4. Handbook of Chemistry and Physics, The Chemical Rubber Co.

UNDERGROUND STORAGE - TWO ATTEMPTS, ONE IN NORWAY AND ONE IN ZAMBIA. A SITUATION REPORT

SUMMARY

An open air museum in the south of Norway planned to make an underground cart-shed underground to save space on their premises.The winter-climate in Norway can be hard with temperatures down to -35°C. The conservator suggested that with good isolation, the temperature in the ground would be stable and high enough to provide a suitable storageclimate without heating. A small,compact airconditioning unit circulate the air and controls the RH level. The store has been in use throughout one winter-season and the result so fare is very promising.

A small provincial museum in the western province of Zambia is supported by the Norwegian development-agency. Unfortunately it was constructed without stoage-facilities. The conservator at the Ethnographical museum in Oslo was connected to the project and suggested an underground storage for the same space saving and climate reasoning, but with quite opposite temperature conditions. Details of these two projects are given in the article.

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The open air museums in Norway. The climatic history of the collections.

The history of the open air museums in this country dates back to the last part of the eighteen century and to the beginning of the twentieth. Traditional rural houses were collected and moved to appropriate sites for reerection. In some cases whole farms with many houses were moved. Objects from every aspect of life were exhibited in these buildings. Since there was no heating they were only open to the public during the summermonths. Usually this meant from june to september. The houses provided nothing but little protection from the outside climate, exept for keeping the objects out of the rain. During wintertime, if the temperature suddenly rises, condensation takes place on the surface of the objects and because the material still has a low temperature rime is formed. Thus sirtain objects, according to the kind of surface, could be covered in ice from time to time. Meteorological readings outdoor in the town where the museum in question is situated shows that the monthly average RH at noon varies between 90 and 63.9 % The temperature varies between - 15 and +10.6 mean. The buildings where the objects are stored or exhibited are made of heavy logs with turf roofing and small windows. This means that they represent a good buffer against the dayly variation in humidity, but still the average RH is very high.

The conservation-condition of objects stored in this way was not so bad. Much of the material has kept remarkably well, especially painted wooden objects. Textiles,paper,upholstery leather etc suffered from attac of sertain microorganisms and there have been problems with corrotion of metal, but the overall state of conservation was not so bad.

Demand for fireproof storerooms and heated exhibitions:

The argumentation for exhibitions which could be open during wintertime, together with the argument for fireproof stores for the colections brought about great changes in the situation. From the early 1960 and onwards, many concrete buildings were erected by the open airmuseums for this purpose. For human comfort both exhibitions and the storerooms were heatet during winter with the result that the RH were down to about 20%. In summer heating was turned of and RH would reach about 60% The dry winterconditions soon prooved to be disastrous for part of the collections and to improve the situation many buildings were fitted with airconditioning. The overall climatesituation in these buildings were not very impressive. Brakdowns, maintenance periodes, malfunctioning control-equipment etc, caused an unstable RH. Furthermore the extreamly low winter-temperatures in this country lead to condensation-problemes in the building-structures when these buildings were humidified during the winter. The damage to the buildings were somtimes severe. Left with the choise between a rapide and dramatic damage to the building and,in the short run,less dramatic damage to the objects,the museum-directors tended to turn of the humidification.

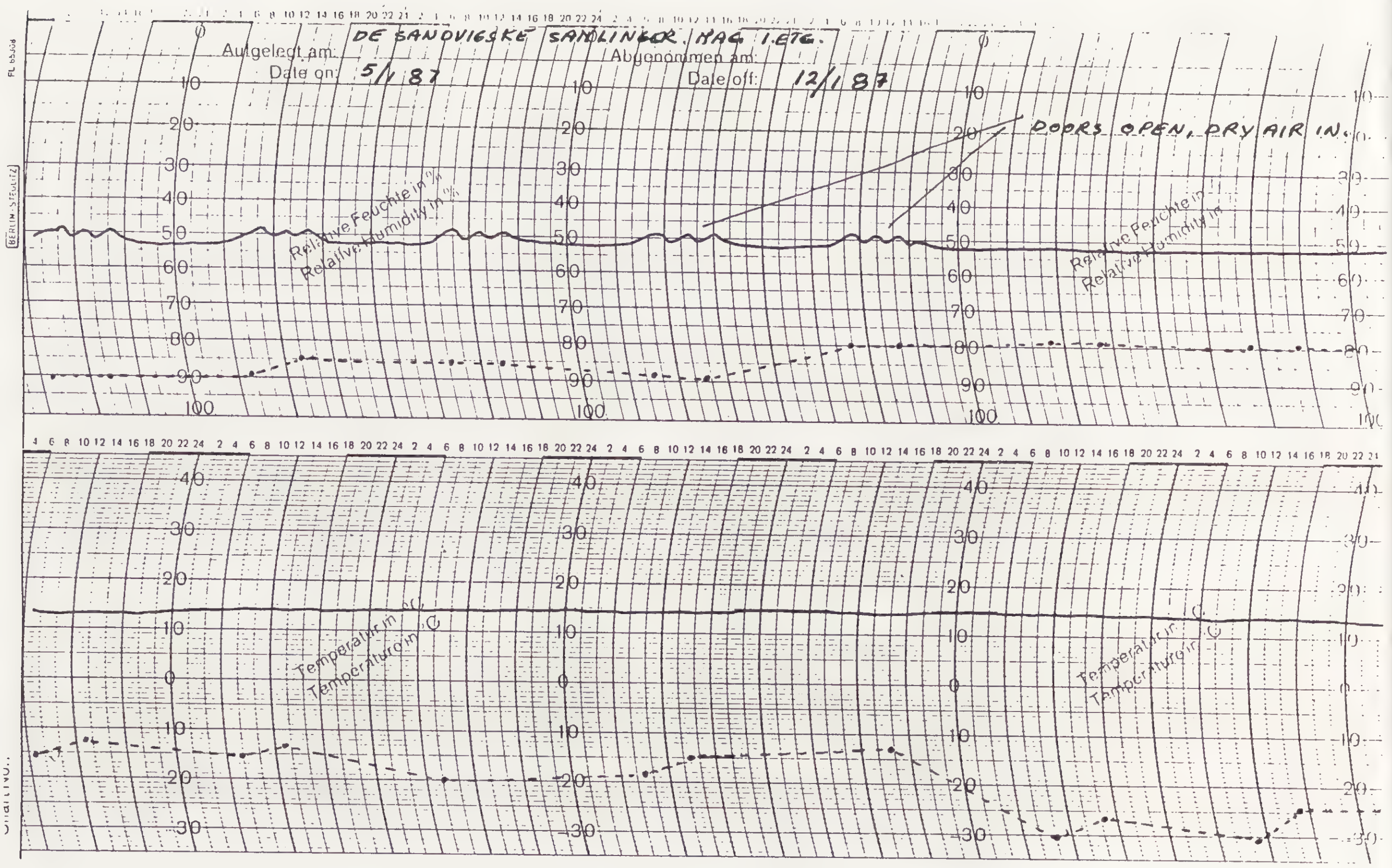
This is the situation for most of the open air-museums in this country today. A large part of their collections are stored and exhibited under conditions that gives great seasonal RH variations. The other part,often the part that contains the large objects, are stored in sheds or barns without climatecontrol like in earlier times.

De Sandvigske Samlinger, Underground storage.

De Sandvigske Samlinger is one of our larger provicial museums situated in the town of Lillehammer north of Oslo. It serves as a district museum for the valley of Gudbrandsdalen. It was founded in 1887 and in the year of centennial celebration it has 130 reerected buildings on the premises. The houses are all made of wood,mainly

log-cabins. The houses are funished in traditional manner and fitted out with utensils from the time they were in use A new administration and exhibition building was put up in 1959. It was planned in a flexible way so that it has been possible to make a series of extentions without altering the characteristcs of the architecture. It was not until the eighties it became feasible to think of further extentions to the museum. The museum director,the late Fartein Valen Sendstad, wanted to build a storage for large objects and horsedrawn vehicles. Neither the space on the premises nor the architecture would allow further extention to the present building. An obvious solution was therefor to build it into the sloping ground behind . He turned to the conservator at the Ethnographic museum for advise on climate and they soon agreed that with the stable temperature in the ground it would be easy to establish a good museum climate at very low running cost. A draught proposal arguing for the use of mother nature to cater for stable temperature and manmade machines to stabilaze the humidity.was put forward and aproved.

The actual building of the store started in 1985 and was compleated in the fall 1986. It is constructed in two separat floors the bottom storey beeing 7-8 m deep in the ground. Each floor cover an area of 900 m^2 and the volume is 2900 cubic meters. Two small aircoditioningplants are fitted in to a ventilation room of 40 m^2. Each unit,of the type Dantherme, operate seperatly and can add or subtract watervapor. They are controlled by humidistates and the air is recirculated via ducts to the whole storage area. A small heating unit of 7 KW can be put on if there is danger of frost. When the store was put into function the autumn of 1986 there was still a lot of uncertainty about the probleme of frost,but during the winter of 1986-87 the temperature has only come down from 20°C in the autumn to 14°C in february 1987. The termohydrograph reading below shows RH and temperature during a particular cold week in January 1987. The outside conditions are plotted in with doted line.



——————— Reccording in the storeroom, bottom storey

- - - - - - - - - - - Data from a wetherstation outside plotted in.

At the time of writing there is no good explanation for the irregularity of the humidity curve, but it has possibly to do with opening of doors during working hours. As part of a research sceme finansed by the department of energy a computerized monitoring systeme was put in. This has been a failure because it has never functioned properly. The equipment is now beeng compleatly changed. When it is functioning it is ging to be very interresting to make comparison

with the cost and efficiency of similar localities above ground.

The result so fare is very promising indeed. No energy has been needed to encrease the temperature and the stabillity of RH is good. Up til now it has never been a change of more than 5%

The argument for investing in such a project has of course been many where security and spacesaving has been very strong. To the conservator any effort to lengthen the life of the objects must be greetet with joy, whatever the selling argument might be. It is sertainly going to be interesting to report on the further development of this project.

Nayuma Museum in the western province of Zambia.

This is a small provincial museum wich is supported by the Norwegian agency for devellopment and cooperation. Unfortunatly the architect did not plan for any storage area. My collegue*and myself from the Ethnographical Museum in Oslo was atached to the project in 1984. During our first visit to the museum it was clear that it would be necessary to rearrange the planning and get storage facilities into the buildingprogramme. In three reports and through cooperation with Gael de Guichen at ICCROM it was finally agreed that an underground storage should be constructed. The main reasoning was that the pressent museum building is a light construction with a thached roof. To make a good storebuilding it would have been necessary to construct a concrete building with very thick walls. This would not have been in correspondance with the architects intentions for the present museum building. Further more the yearly average of 60% RH 20^{o}C. suggested that the contitions underground*around that figure. Above ground a similar construction to the present museum can be used as workshops.

* Mr Harald Beyer Broch Sosial antropologist.

*vould stabilze

The underground store cowers an area of 144 square meters with a volume of 360 cubic meters. An airhandeling unit,Dantherm CD 1700, is beeing installed within the storeroom. At low RH the unit starts humidifying and stops at a preset level. The same applies whwn humidity is to high. Dehumidifying starts and stops at a preset level. The unit is fitted with fresh water-supply and connected to drains. For airmovement there are two wallmounted oscilating fans. There is an air inlet in one end and an outlet in the other. The outlet is connected to an airduct wich ends high above the ground. This is meant to evacuate eventual gases in case the need for fumigation of the store rises.

Conclution:

The small active systeme for the large storage area in Norway has prooved to be reliable trough one hard winterseason.
The passive systeme at Nayuma is beeing put into function at the time of writing.
We think that this projects will lead to some very interesting devellopment for low cost storage methodes.

SUMMARY

A cost evaluation has been made of the maintenance of 13 DEFENSOR 2000-V humidifyers. The reliability depends strongly on wether the apparatus is properly and regularly cleaned. Any neglection of this involves the breakdown of expensive spare parts. The use of deionised water decreases the costs considerable.

MAINTENANCE OF THE DEFENSOR 2000-V

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Introduction

When the institute was build in 1962, all restoration workshops were equiped with fully automized climate control units. The maintenance of the building, as all governmental properties, is a responsibility of the Ministry of Public Works. This means that nobody of the staff of the institute has any access to the machinery. Whenever any non desired temperature or relative humidity is observed, this has to be reported to the ministry, housed in another building. Depending on the good will, the budget or any other reason, an intervention takes place within one day, one week or one month.
Some years after the installation the maintenance was completely stopped: dust filters were no longer replaced, sprinklers decalcified, pumps revised. The result was that the climate in the workshops was no longer stable but fluctuated in summer time according to the wether conditions, while in winter time the heating caused extreme low relative humidity.
As no short term solution to the problem could be expected, it was decided to equip the workshops with air humidifiers.
Because of the good reputation, 13 DEFENSOR-2000V apparatus were bought over a period of 4 years. The inventory numbers, cost-price, date of purchase and destination in the institute are listed in table 1.

Table 1; list of DEFENSOR 2000-V humudifiers

Inv.numb.	date of purchase	cost price (BF)	destination
5886	28/05/79	29.055	polychr.sculpt.
5887	28/02/79	29.055	storage room
5969	26/09/79	28.937	paintings
5970	26/09/79	28.937	textiles
5971	26/09/79	28.937	paintings
5972	26/09/79	28.937	paintings
6089	27/10/81	30.771	storage room
6090	27/10/81	30.771	paintings
6109	21/01/82	30.637	polychr.sculpt.
6110	21/01/82	30.637	polychr.sculpt.
6111	21/01/82	30.636	polychr.sculpt.
6119	5/05/82	41.744	laboratory
6120	5/05/82	41.744	textiles

Defensor 2000-V

The Defensor 2000-V is an evaporative humidifier (fig.1). The air is sucked through air intake grids with filter mats (I) and blown through a humidified mat (II). This is carried by a plastic drum (III), which dips into a reservoir of water (IV). A small fan (Fig.2 n°2) blows air over a hygrostate (Fig.2 n°3), which stops the air circulation automatically when the desired humidity is obtained. The drum rotates continuously, even when the air circulation is stopped. A water level indicating bar (Fig. 2 n° 4) shows continuously the water left in the reservoir and stops the engine when it runs out of water. The technical data of the DEFENSOR 2000-V are summarized in table 2.
Each apparatus is sold with a "Maintenance Instructions" leaflet and a very detailed spare parts list.

Table 2: Technical data of the DEFENSOR 2000-V

- Control voltage	220 V 50Hz ± 10%
- Power consumption	50 Watts
- Evaporating capacity	19-45 ltr/24 h 0.8-1.9 ltr/h
- Room capacity	up to 250 m³
- Air circulation	
stage 1	280 m^3/h
stage 2	350 m^3
- Room air temperature	+5°C - +40°C
- Room air humidity max.	70%

Installation

Before the first installation, each apparatus was allowed to work for two days and then the humidistat was checked: by turning slowly the control knob up and down a slight click indicates at which RH the apparatus starts working. This is supposed to be the RH of the surrounding air. Although most of the humidistats worked correctly, some showed a deviation of up to 20%. This can easily be corrected by removing the upper part of the control knob, unscrewing the nut and adjusting the knob.
Then the apparatus were placed in the workshops. The filling, with tap water, was done by the conservators. The apparatus nr. 6199 (lab), used to humidify silicagel, has only be filled with deionised water. No proper maintenance programme was elaborated in the beginning.

Maintenance

In the beginning of 1983, several humidifiers started breaking down. It therefore was decided to appoint a responsible person to take care of all repairs and a regular maintenance.
According to the Maintenance Instructions the cleaning should be carried out every 4 weeks. For 13 apparatus this means a full time job for 1 person, which was technically impossible.
Therefore a maintenance plan was set up, consisting in a thouroughly cleaning of each apparatus at least 3 to 4 times a year.
The cleaning consists in:

- removing and vacuum cleaning of the 4 dust filter
- removing the humidifying mat and dissolving the scale of minerals precipitated from the tap water.
- cleaning of the drum, eventualy removing the deposited lime
- cleaning of the water basin and float system
- checking all the iron parts for rust formation, if necessary followed by a rust blocking treatment
- replacement of all defective parts

Depending on the amount of deposited lime and rust, a complete cleaning takes 1 to 2 days.

Main problems

Gear wheel:

The main problem encountered at the first maintenance was a complete wearing down of the gear wheel, supporting the drum. Due to the fact that the humidifying mats were not regularly enough replaced, the drum became to heavy and started rubbing the gear wheel. This became so thin that the cogs no longer fitted into the cogwheel of the drum, which stopped turning.
Except apparatus nr. 6119, all gear wheels have already been replaced at least once (table 3).

Synchromotor

Whenever the apparatus works too long with a humidifying mat loaded with lime, this causes not only a wearing of the gear wheel, but also an important strain on the axes of the gear box of the synchromotor. Several of those gear boxes broke down. As the synchromotor and gear box are sold in one piece, the whole system had to be replaced, although the motor itself was still perfect.

Fan:

In two of the apparatus the small fan got loose and had to be replaced. This seems to be rather accidental.

Water basin:

The water basin has to be filled from the front side of the apparatus. The plastic tank is opened by putting a special support on the centre of the water basin and against the appliance housing. This makes the front wall of the basin to protrude. The weak point of the whole system is the special support. As long as this is used, no problems seem to occur. For three apparatus it has been lost and replaced by wooden sticks.

As the original support is rather short, the filling takes some time and is not very easy, so the new supports were made a little longer. Although there was only a slight difference in length between both,the water basins became very fast damaged. The increased strain during the filling made them tear up. Replacement showed to be extremely expensive (± 5.000BF), so it was decided to use adhesive tape, which seems to work quite well although regular replacement is necessary.

Drum:

After some years of using tap water, lime started precipitating on the plastic drum. Because experience had shown that any increase in weight of the drum or humidifying mat can cause damage to the gear box, it was decided to remove this lime crust, even if it had no direct influence on the effectivness.
Because of the extremely good adherence the removal caused scratches onto the surface. These increase the precipitation of lime so that one arrives in a vicious circle: removing lime causes damage to the drum which increases the precipication of lime which needs more removing of lime...

Humidifying mats

Depending on the maintenance and the hardness of the water, humidifying mats can be used for 2 to 5 years. In general the mats support quite well a regular cleaning with dilute hydrochloric acid. It has however been marked that the quality of the mats bought recently is inferior. After 2 to 3 cleanings, they stretched so that they had to be shortened to fix on the drum.

Rust:

Rust formation depends mainly on the daily maintenance. Apparatus which are filled very carefully, without any water spoiling, show no problem, even after 8 years.
When the addition of water is carried out with less care, the support under the water basin starts rusting. Three apparatus show severe rusting under the water basin so that in the near future a stability problem will raise. In one apparatus, the round grids had to be replaced.

Use of "MICROPUR" tablets

The manufacturor of the humidifyers delivers with each apparatus a sample of Micropur tablets for water preservation. The use of such tablets seems to be absolutely necessary. Two apparatus have been working for several months without addition of these tablets. The drum and the humidifying mat became covered with a colourless jelly. Under the microscope, unicellular organisms could be observed. The destruction of this jelly seems to be difficult: although at each maintenance all parts which have been in contact with water are cleaned with a dilute solution of hydrochloric acid, the jelly appears each time again, even when Micropur tablets are used later on.
No information is available on the possible health hazard of micro organisms expelled by the humidifyers.

Table 3: Maintenance problems of the Defensor 2000-V over a period of 7 years

Inv.numb.	replaced parts	main problems
5886	1 gear wheel. filters, mat	rust
5887	2 gear wheels, 1 motor, filters, mat,	rust, jelly
5969	2 gear wheels, 1 vent, 1 fan, mat	-
5970	1 gear wheel	-
5971	1 motor, 1 set of profiles bars, mat	-
5972	1 gear wheel, 1 fan, mat	-
6089	1 gear wheel, 1 motor, mat	jelly
6090	1 gear wheel, mat, filter	-
6109	2 gear wheels, water basin. mat	-
6110	1 gear wheel, 1 motor, 1 fan, filter mat	rust
6111	2 motors, mat, filters	
6119	-	-
6120	2 gear wheels, mat	

Conclusion:

The DEFENSOR 2000-V proved to be a suitable apparatus for stabilizing the relative humidity in restoration workshops. Figure 3 shows a recording of the temperature and R.H. in the polychrome sculpture workshop which is equiped with 2 Defensor 2000-V apparatus. It has however taken into account that a strict cleaning programme has to be followed in order to keep it properly working. Without any regular maintenance expensive repairs will be necessary after a few years. Up to now an amount of 80.000 BF has been spend to keep 13 apparatus properly working for 7 years. This does not include a half-time manpower.
The use of deionized water is advisable. The apparatus in the laboratory worked continuously for 5 years without any breakdown. Even the original humidifying mat is still in perfect condition.

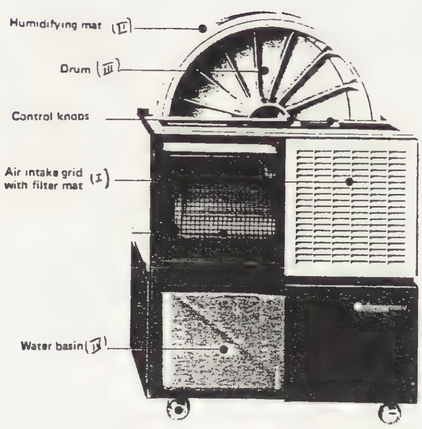

Figure 1: DEFENSOR 2000-V

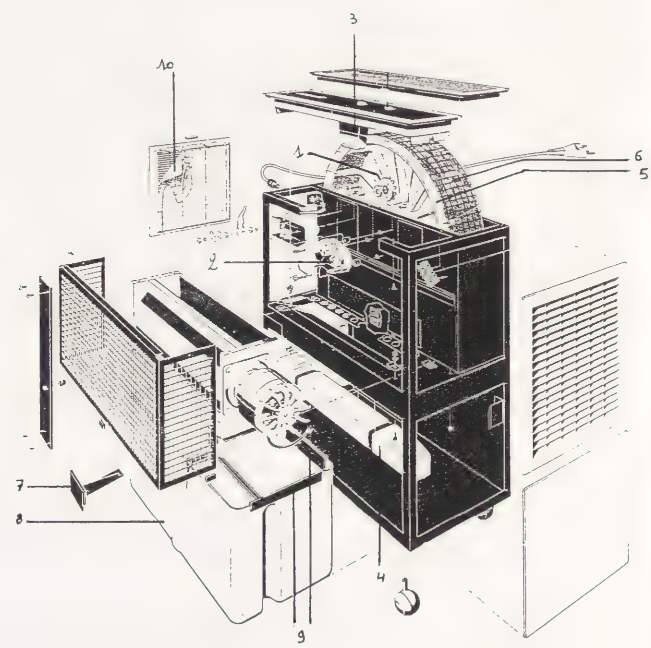

Figure 2: Spare parts which need replacement or special care.
1: gear wheel
2: synchromotor + fan
3: humidistat
4: water level indicator
5: drum
6: humidifying mat
7: support
8: water basin
9: round grids
10: dust filters

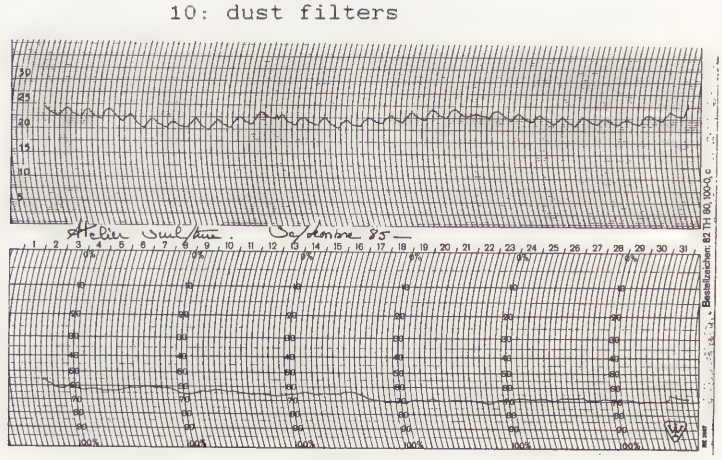

Figure 3: Temperature and R.H. in the workshop of polychrome sculpture

SUMMARY

The influence of silicagel on the acidity of air in a show-case is investigated. Out of three types, one seems to give a potential danger of decreasing the pH. Extraction of the water soluble salts, present in the silicagel is possible but does not seem to influence the acidity.

THE PRESENCE OF SOLUBLE SALTS IN SILICA GEL

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Introduction

The use of silicagel for the stabilization of the relative humidity in show-cases is well known (1, 2, 3). On request of Mr. Gaël de Guichen, coordinator of the ICOM Conservation Committee Working Group "Control of Climate and Lighting" our laboratory looked into the problem of the presence of soluble salts in silicagel. The presence of such salts, when derived from strong acids or bases, could indeed influence the pH of the surrounding air and thus have a harmful effect on the objects on display. The problem was first raised by L. Agati (4) when he found an important amount of chloride ions in a show-case conditioned with silicagel (4).

Analysis

Three different types of silicagel have been investigated:

I: Silicagel Uetikon, Type Blaugel E
Supplied by: Chemische Fabrik Uetikon
CH-8707 Uetikon, Switserland

II: Silicagel Uetikon, Type E
This silicagel is identical to n° I, but without indicator. Both products are described by the manufacturer as "Chemically inert, withouth odor or taste, perfectly non-flammable, stable towards acids and alkalies (except hydrofluoric acid and concentrated bases).

III: Art-Sorb Bead Silicagel
Supplied by:
Fuji-Davision Chemical Ltd, Japan

1. Extraction of soluble salts

A quantity of 10 grams of silicagel, conditioned at 55 % R.H., was extracted with 100 ml of deionised water by shaking the mixture for 1 hour. After filtering, qualitative tests on anions and cations have been executed. The results are summerized in table 1. As it was not possible to identify any cation in silicagel n° III, neither with the classical identification tests nor by means of an electronic microprobe ; an emission spectrum in acetylene-air flame, between 200 and 860 nm, has been recorded. This allowed to identify the presence of lithium.

Table 1: Qualitative analysis of the extractions

	n° I	n° II	n° III
chloride	++	±	+++
nitrate	±	±	±
sulfate	++	+++	±
sodium	+++	+++	+
potassium	+	+	±
lithium	+	-	+++
calcium	+	-	+
magnesium	-	-	±
cobalt	++	-	-
aluminium	-	-	+
pH	3.68	3.25	6.27

Legend: -: not present
±: traces
+ to +++: increasing amount present

The results show that silicagels n° I and II contain, besides $CoCl_2$ as indicator, also an important amount of Na_2SO_4. Silicagel n° III contains only LiCl. This product is obviously added to increase the water absorption capacity of the material and to allow the product to stabilize the air humidity at low values. It is indeed known that the air, in equilibrium with a saturated solution of LiCl, has a relative humidity of 12 % at room temperature. Measuring the pH of the extracting solutions revealed that n° I and II contain a certain amount of acid. The extraction liquid of the silicagel n° III is almost neutral.

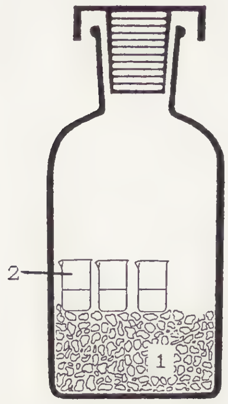

Figure 1: Testing of the influence of preconditioned silicagel on the surrounding air.
1: silicagel conditioned at 95 % R.H.
2: vials containing acid-base indicators.

2. Influence on the pH of the surrounding air.

In order to see if the salts, present in the silicagel have any influence on the air conditioned by it, 100 g of each product has been conditioned at 95 % R.H. by placing it for 6 days in a sealed glass container with a large quantity of water.
Then each silicagel was brought into a recipient of 500 ml together with three beakers of 25 ml containing each an acid-base indicator (fig. 1). The indicators used are summerized in table 2. A reference vial was prepared containing a solution of pH 4.2 of hydrochloric acid.

Table 2: Indicators used in the test vials.

Vial content	indicator			
Silic. n°I	universal	bromophenol blue	congo red	-
Silic. n°II	universal	bromophenol blue	congo red	-
Silic. n°III	universal	-	-	aliz. red
HCl, pH 4.2	universal	bromophenol blue	congo red	-

After 14 days of exposure, no single indicator changed color. That the technique works, was proved by placing a beaker of 25 ml filled with a universal indicator and another one with alizarine red S at the open air for 14 days: they both were transformed into their basic form.

Two supplementary vials were then prepared: one with a solution of 7 % acetic acid, the other with a solution of hydrochloric acid of pH 4.2. In the former the three indicator solutions were placed, together with three ribbons of filter paper, impregnated with the same solutions, which were suspended at the stop cork. In the latter, only the three ribbons of impregnated paper were suspended. After some hours all the indicators started changing color in the beaker containing acetic acid, after one day all the indicator solutions were in the acid form.
In the beaker containing the solution of hydrochloric acid, no change could be observed.

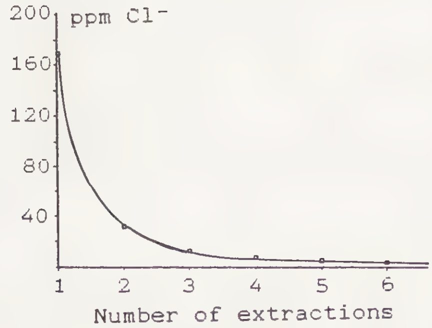

Figure 2: Extraction of Cl⁻ from silicagel n° I

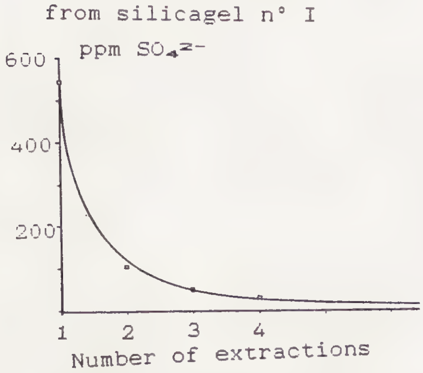

Figure 3: Extraction SO_4^{2-} from silicagel n° II

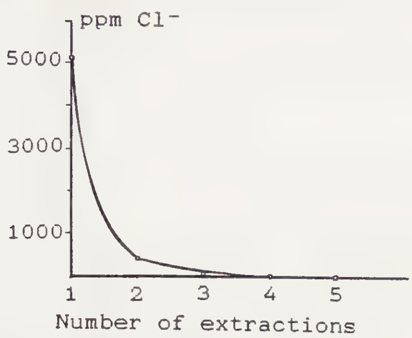

Figure 4: Extraction of Cl⁻ from silicagel n° III

<u>Artificial aging</u>

In order to speed up an eventual release of acid or alkaline products, all the test vials were submitted to a temperature program consisting of 2 hours at 35°C followed by 1 hour at 10°C. In this way, any volatile product present in the silicagel would evaporate and subsequently condensate onto the indicators. The cycle was repeated 56 times. After 16 cycles, the Congo Red S in the vial with silicagel n° II showed a very slight discoloration towards the acid form. At the end of the aging, the other indicators did still not show any color change.

<u>Extraction of soluble salts</u>

In order to see if it is possible to extract the remaining salts and acidity out of the silicagel, 10 g of each product has been extracted for 1 hour with 100 ml of deionized water. After this period, the water is decanted and replaced. The operation has been repeated six times, after which all the solutions have been analysed: in the solutions from silicagel I and III the amount of chloride ions has been determined, in the solutions from silicagel n° II the sulfate ions have been dosed. The results, in mg of ions present in 100 g of silicagel, are summerized in figures 2, 3 and 4. The acidity of all extraction solutions is listed in table 3.

Table 3: pH of the extraction solutions

Extraction n°	silicagel n°I	silicagel n°II	silicagel n°III
1	3.61	3.12	6.25
2	4.19	3.70	6.90
3	4.48	3.94	8.25
4	4.84	4.06	8.56
5	4.81	4.15	8.69
6	4.84	4.35	8.52

The extraction of the soluble salts seems to be no problem, as almost all salts are removed after one extraction. It is however surprising that this operation does not seem to have any influence on the acidity of silicagels n° I and II.

Conclusion

- The three silicagels under investigation contain a certain amount of water soluble salts ($CoCl_2$, Na_2SO_4, LiCl). The silicagels n° I and II contain also a residual amount of acid.

- For at least one of the silicagels there seems to be a potential danger of acidification of the surrounding air at high relative humidity.

- The soluble salts can easily be extracted, but this seems to have no influence on the acidity of silicagels n° I and II.

- As the physical structure of silicagel can be changed when it is brought into contact with liquid water, it is necessary to check if this operation has an influence on the absorption-desorption capacities. This point is still under investigation.

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PROPRIETES ANTI-U.V. DES FILMS DE SECURITE

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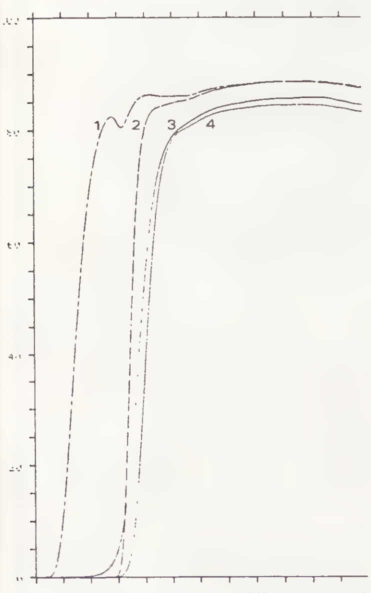
RESUME

L'étude après vieillissement des propriétés anti-U.V. des films de sécurité nous éclaire sur la disparité des produits qui peuvent nous être proposés comme filtre. Sur 10 échantillons, après 1800 heures de vieillissement artificiel, il ne reste plus que 6 produits répondant au standard. Un classement par un label de 3 caractères, chacun indiquant une classe (A, B ou C) permet une notation aisée de ces matériaux.

Courbes spectrales de filtres anti-U.V. montés sur verre



1. Glace float de 6 mm
2. Glace feuilletée (44.2) avec intercalaire de Monsanto
3. Laque antisolaire
4. Film de sécurité (classement AAA)

Introduction

Il n'est pas nécessaire de revenir sur l'importance que peut avoir pour la préservation des oeuvres, la suppression du rayonnement U.V. L'éclairage naturel étant de loin le plus dangereux mais aussi celui qui nous permet les mises en valeur les plus fidèles. Rien de plus normal que de rechercher des solutions qui exploitent ses avantages tout en neutralisant ses inconvénients. Dans un bâtiment existant le recours aux films de sécurité, dits aussi de protection U.V., fait partie de ces solutions. Ces films sont utilisés depuis plusieurs années, sans que l'on connaisse avec certitude l'évolution de leur efficacité dans le temps, nos fournisseurs ne disposant eux-mêmes que peu de renseignements à ce sujet. Seuls Lafontaine R.M. et Maclead K.J. ont publié une enquête à ce sujet.

Le vieillissement naturel est sans aucun doute le plus juste d'enseignements, mais les résultats n'en sont pas toujours exploitables, car en l'espace de quelques années un produit peut être modifié ou retiré de la vente. Le vieillissement artificiel, s'il ne peut prétendre à une reproduction exacte du comportement de matériaux, en milieu naturel, nous permet de comparer différentes fabrications et de fournir aux utilisateurs les conseils rapides qu'ils demandent.

Etude

1. Collecte des échantillons
Les films choisis pour l'étude sont vendus dans le commerce comme films de sécurité contre le bris du vitrage. Mais les fabricants ajoutent qu'ils pallient aussi le rayonnement U.V.
RICHNER 2854, 2884, 69894, 2881
SOLAR CLX400, CLX 200
SOLAR ISOL UVPS 200, UVPS 400
3M P 70
VALVAC CLX 400

2. Préparation des éprouvettes
Les éprouvettes sont constituées d'une glace de dimension 10 x 10 x 0,6 cm et du film appliqué. Découpé en deux morceaux l'un de 10 x 7 x 0,6 cm à vieillir, l'autre de 10 x 3 x 0,6 cm servant de test à l'état neuf.

3. Vieillissement
Vieillissement accéléré dans une enceinte ATLAS 25 F équipée d'un brûleur Xénon de 2500 W, muni de filtres absorbant le rayonnement U.V. en dessous de 300 nm. Durée totale du vieillissement 1800 heures à HR 50 % $\pm$ 5 et température 20° $\pm$ 2°.

4. Méthode d'analyse
Spectroscopie U.V. visible par transmission sur spectromètre PERKIN ELMER type LAMBDA 5 avant vieillissement puis toutes les 400 h jusqu'à 1800 heures.

5. Interprétation des courbes
Comparaison des pourcentages de transmissions aux longueurs d'ondes suivantes : 320, 380, 400, 420, 550, 700 nanomètre.
320, 380, 400 et 550 nm sont les longueurs d'ondes qui entrent dans la norme présentée par Garry Thomson soit : est considéré comme filtre U.V. le filtre qui laisse passer moins de 1% du rayonnement U.V. à 320 et 380 nm, moins de 50% à 400 nm, étant entendu que ces valeurs sont définies en fonction d'un maximum égal à 100% à 550 nm.

420, 550 (560) et 700 nm sont les longueurs d'ondes utilisées en colorimétrie pour la mesure de l'indice de jaunissement d'un matériau après vieillissement.

6. Exploitation des résultats
A partir de ces résultats, il est possible de constituer un classement des différents films qui tiendra compte de leur efficacité vis-à-vis :

1) de leur pouvoir anti U.V.
2) de la qualité et quantité de transmission de la radiation visible.

Nous proposons pour la réalisation de ce classement un label de trois critères :
- transmission U.V. état neuf chacun comportant une classe définie
- transmission U.V. après vieillissement
- transmission visible après vieillissement

comme suit :

la valeur à 550 nm étant la transmission de référence (100%)

Premier critère : transmission U.V. avant vieillissement
Classe A :
- transmission ≤1% pour > = 320 nm
- transmission ≤1% pour > = 380 nm
- transmission ≤50% pour > = 400 nm

Classe B :
- transmission ≤ 1% pour > = 320 nm
- transmission ≤ 5% pour > = 380 nm
- transmission ≤ 55% pour > = 400 nm

Classe C :
- transmission > 1% pour > = 320 nm
- transmission > 5% pour > = 380 nm
- transmission >55% pour > = 400 nm

Second critère : transmission U.V. après vieillissement
classe identique à précédemment

Troisème critère : transmission du visible après vieillissement
variation de la transmission visible après vieillissement mesurée à 420, 550 et 700

Classe A somme des 3 variations ≤ 5%
classe B somme des 3 variations ≤10%
classe C somme des 3 variations ≥10%

Suivant le classement, nous pouvons, à partir des films testés obtenir le tableau ci-dessous :

Produits	Transmission Etat 0 en %						Transmission Etat 1800 en %						Label
	320	380	400	420	550	700	320	380	400	420	550	700	
Valvac CLX 400	.1	40	71	78	83	79	.1	44	74	76.5	80.8	76.5	C C B
Richner 2854	0	0	30	72	85.2	80.5	0	1	40	70	82.8	79.2	A A A
Richner 2884	0	0	35	74	85.5	80.5	0	17	60	74	82.5	80	A C A
Richner 69894	0	0	15	71	85	81.5	0	0	15	62	72	70.5	A A C
Richner 2881	0	0	15	67.5	82	78	0	0	15	67.5	81	79	A A A
Solar X CLX400	0	.5	39	78	85.6	78.9	0	1	39	79	84.8	78.9	A A A
Solar X CLX200	0	.5	38	78	86	79	0	.5	38	74	83.6	78	A A B
Solarisol UVPS400	0	.1	39	75	85	84	0	.5	40	73	82	82.5	A A B
Solarisol UVPS200	0	5	62	80.5	80.5	84	0	10	64	80	80	84	C C A
3 M P70	0	1	43	77	85.5	84	0	2	46	74	82	81.8	A B B

Conclusion

Ces films sont avant tout destinés à la protection contre le bris des vitrages. Bien qu'annonçant une protection vis-à-vis du rayonnement U.V. leur qualité est très inégale dans le temps.

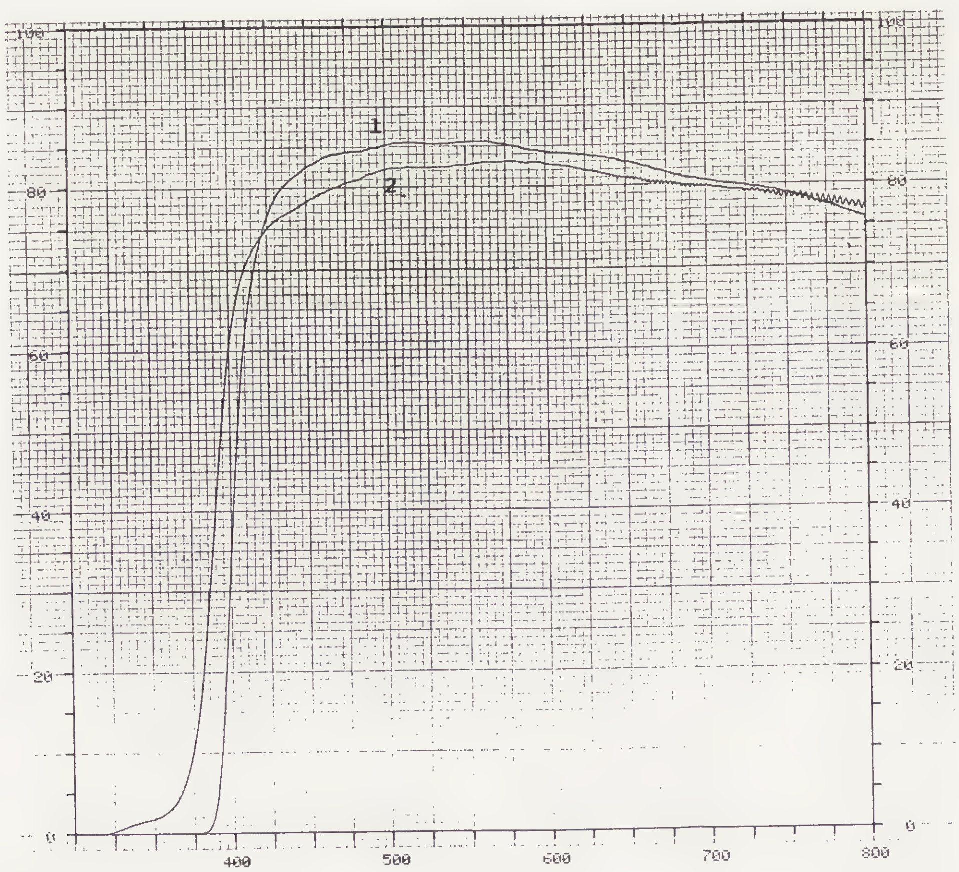
Les facteurs de variations peuvent être induits par la nature et l'épaisseur du film, par la nature de la colle et des agents anti U.V. additionnés à l'un ou/et l'autre, d'où la nécessité maintenant d'identifier par chaque matériau testé la nature exacte de chacun de ses composants afin de pouvoir élaborer un cahier des charges précis vis à vis des fabricants et de mieux préjuger des produits nouveaux.

Après 1800 heures, 4 films ne correspondaient plus au standard, 3 autres n'accusaient pratiquement pas de variations, 3 sont moyens au niveau du visible. Parmi ces trois derniers l'un affirme une excellente stabilité dans le domaine des U.V. mais un net affaiblissement de la transmission lumineuse. Ce phénomène est dû à une transformation des chaînes macro-moléculaires de la colle ou du film et semblerait d'une importance toute relative (compensation par diffusion de la perte par transmission).

Une prolongation de la durée du vieillissement, suite à ces résultats est à envisager, jusqu'à 3000 heures.

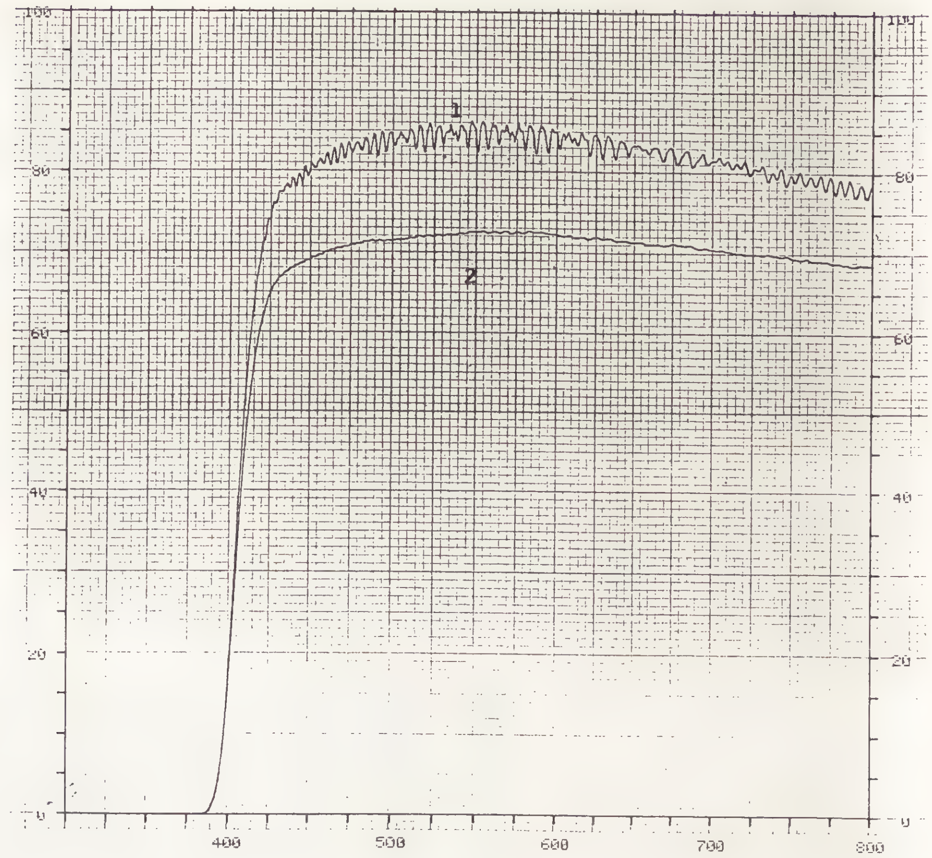
ANNEXE

Exemple de classement de 3 films de sécurité

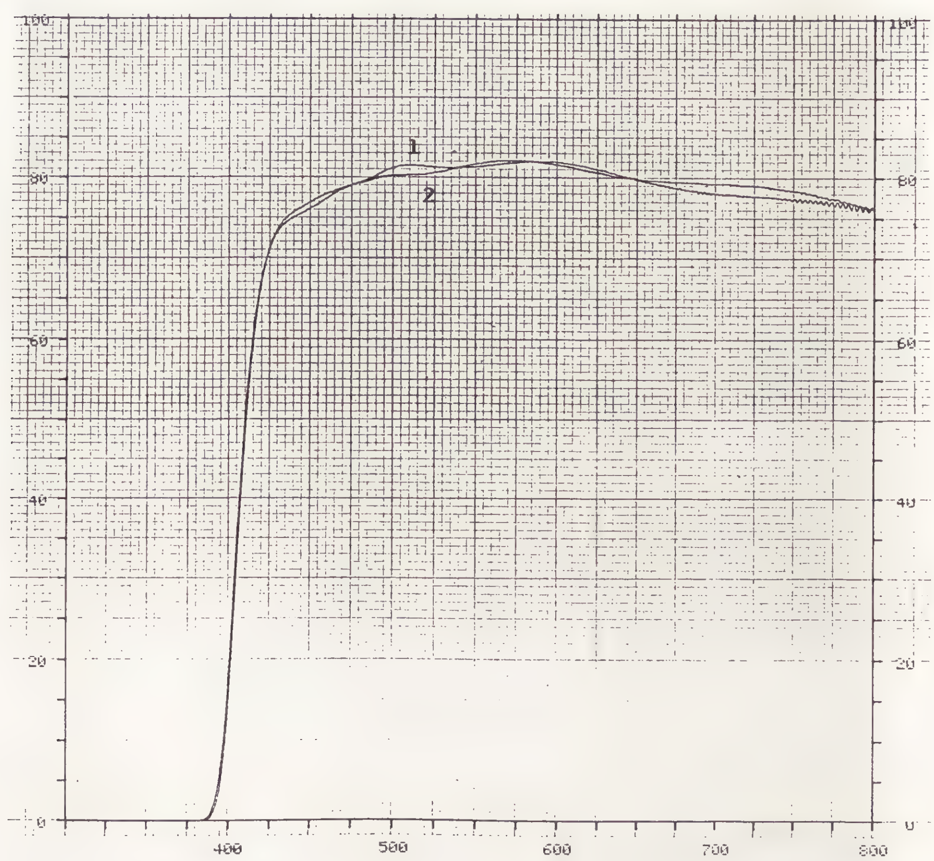


Film RICHNER 2284

1. Avant vieillissement
2. Après vieillissement
   classe ACC



Film RICHNER 69894
1. Avant vieillissement
2. Après vieillissement classe AAB



Film RICHNER 2881
1. Avant vieillissement
2. Après vieillissement classe AAA

SUMMARY

This study was conducted to investigate alternatives to the RH buffers used in an enclosed space, such as silica gels and Nikkapellet. Various agricultural products and also some industrial products were tested for their equilibrium moisture content, their specific moisture reservoir, and their response time to the change of relative humidity in the environment. Some of these materials were applied to experimental showcases, and the specific moisture reservoir was deduced. The result of a series of experiments showed that the agricultural products may be applied to showcases as a RH buffer, but that the specific moisture reservoir should be studied with the relationship between the air leakage rate of the showcase and the response time of the buffering material.

A STUDY OF NATURAL MATERIALS AS RH BUFFERS AND APPLICATION TO A SHOWCASE

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Introduction

It is generally accepted that a high degree of RH stability contributes to the conservation of cultural property. With standing this point of view, many studies on exhibition cases and buffering materials such as silica gels and Nikkapellet have been done. Conservators and curators have been mostly conserned with the amount of the sorbent necessary to reduce RH fluctuations inside showcases and with the sorbent's most effective application. We still need to progress in these areas both theoretically and practically.

However, these commercial sorbents are not available everywhere especially in developing countries and they are too costly for poor museums. As a result, insufficient amounts of silica gel are placed beside objects in showcases. It seems worth while to try to find substitute of silica gels among the natural materials and agricultural products surrounding us. It is preferable to use sufficient amounts of natural materials as buffer than to use uneffective amounts of silica gel. When used neglectfully, these organic and natural materials are subject to insect attack, thus causing the biodeterioration of the objects which they are meant to conserve. This aspect must always be kept in mind.

ICCROM has encouraged the study on the use of natural materials as RH buffers and the author shares this view. The purpose of this study is to take a small step in this direction by experimental and theoretical work.

Fundamental principles

Every natural material has a property of absorption and desorption of moisture from surrounding air. After a material has been kept under a certain RH until equilibrium is established, its moisture content can be calculated to the dry weight. This is called the equilibrium moisture content(EMC). As it is measured under a constant temperature, it is also termed the isotherm.

The specific moisture reservoir(SMR) is derived from the EMC curve and it represents the amount of water lose or gained, in grams, by one kilogram of buffering material when the ambient RH increases or decreases by one percent. A higher value of SMR indicates a higher buffering efficiency.

The EMC for the absorption process does not follow the EMC for the desorption process. This phenomenon is termed hysteresis and the area where the two curves have different EMC values is called the hysteresis loop. The SMR from the absorption process is different from the desorption's one within the hysteresis loop.

The speed, that is the response time, of the moisture movement between the materials and the atmosphere is also of interest. When the RH within a showcase is suddenly changed, the sorbent will begin to emit or absorb maintained close to the initial level. Miura(1) has studied this phenomena by observing the time taken to back up to the initial RH with various amount of sorbents. We can understand this response time by observing the diffusion of moisture in the material(2). Comparison of the diffusion rates between materials ranks the materials according to the rate of their response to the RH changes.

Thomson(3) explained that the RH change within showcases is one of the exponential decay, and it can be characterized by a hygrometric half-time. The hygrometric half-time of the case is the time taken to reach the half way RH which exists between the initial case RH and the ambient RH. The hygrometric half-time depends on the case contents, which are the buffering material and exhibition objects, and on the rate of air leakage. The rate of air leakage of the case is measured as the number of air changes per unit time. The equation of the exponential decay and the relationship between the half-time and the air leakage rate is expressed as follow:

$$\frac{C - R}{C_0 - R} = EXP(-kt) \quad \text{Equ(1)}, \qquad t = \frac{0.693}{k} \quad \text{Equ(2)}$$

where C is the case RH, R is the ambient RH, C is the initial RH, t is the half-time of the decay without any buffer, k is the air leakage rate of the case, and t is time. Addition of the buffering material can extend the half-time. This relationship is given by Thomson(3) in the following formulae:

$$t^* = \frac{0.693}{k^*} \quad \text{Equ(3)}, \qquad k^* = \frac{kW}{W + MB} \quad \text{Equ(4)}$$

where W is the amount of moisture in grams, which is gained or lost in a cubic meter of air within the case for one percent RH change at temperature T. M is the SMR of the buffer, B is the weight of the buffer in kilograms in a cubic meter of air, k* and t* are the new rate of air leakage and half-time respectively.

Two type of RH fluctuation may exist in nature. One is daily fluctuations of outdoor RH and the other is seasonal fluctuations of outdoor RH. The case RH might change with them. To reduce and slow down the case RH change to a reasonable degree, Thomson(3) proposed to extend the half-time of the case to half a year or half of the annual cycle. This simple proposal can be also applied to the daily RH change. If the half-time of the showcase is extended to more than 12 hours or half of the daily cycle, the change of case RH is reduced considerably.

Experimental

1. Tested materials

The following natural materials were tested in this study for their EMC, their SMR, and their response time:

1) rice seed
2) wheat seed
3) ground wheat (0.5mm diameter)
4) wheat flour (very fine powder)
5) soy bean
6) rice capsules
7) buckwheat capsules
8) wheat straw
9) Blackwood African (Dalbergia melanoxylon)
10) spruce

These materials were obtained commercially, and they have not received any chemical treatment. In addition to these natural materials, the following products were also tested:

11) charcoal
12) rabbit glue (bead type, 3mm diameter)
13) flax fabric
14) calfskin leather (2mm thickness)
15) casein (fine powder)
16) carboxy methyl cellulose (fine powder)
17) Dydrargil (1mm diameter)
18) Regular density silica gel (3mm diameter)

2.1. Measurement of equilibrium moisture content

To measure the EMC of materials, seven atmospheres of different RH were prepared in glass vessels. A constant level of relative humidity was maintained by means of saturated solutions of chemical salts. Adopted RHs and chemical salts are listed on Table 1. The dry weight of the materials was obtained by placing them over phosphorous pentoxide within the glass vessel until a constant weight was obtained. After the dry equilibrium point was obtained, the moisture content of the materials was determined gravimetrically through treatment in a series of atmospheres where the RH was increased from 20% to 80%. When 80% RH was reached, the measurement was repeated in a series of decreasing RH atmosphere until 20% RH was reached. The materials were kept in each atmosphere for 48 hours. The temperature changes experienced during each measurement of EMC were around 2°C.

TABLE 1. Relative humidity versus temperarure for saturated chemical solutions(4)

Temperature (°C)	CH_3COOK	$MgCl_2 6H_2O$	$K_2CO_3 2H_2O$	$Mg(NO_3)_2 6H_2O$	NH_4NO_3	NaCl	KCl
15	24	33	43	56	68	75	86
20	23	33	43	55	65	75	85
25	22	33	43	53	62	75	85
30	22	32	43	52	59	75	84

(%)

2.2. Discussion

Typical examples are plotted in Figure 1. The SMRs of the materials are summarised in Table 2. The table shows that most natural materials are included in the region where the SMR value is of about one within an atmosphere where the RH measures between 30% and 70%. Even if we use 20 kg/m of the natural material the half-time is extended to only 90 days or less when the air leakage rate of the case is about one per day. Is this half-time valid or meaningless to preserve the object within the showcase or the enclosed space. With regard to this point, a wooden box for storage, in which picture scrolls and paper documents have been preserved traditionally for 500 years or more in Japan, suggests an interesting fact. Miura(4) studied this wooden box

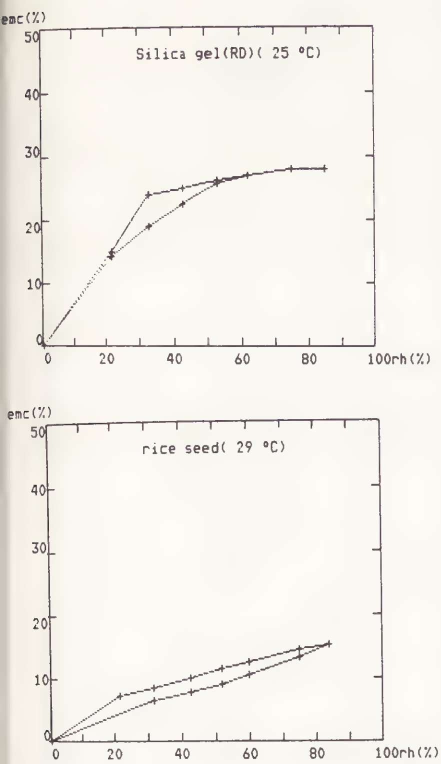

Fig.1 Equilibrium moisture content/Relative humidity plots for silica gel and rice seeds

and gave the results of moisture movement between the inside of the box and the ambient air. The author calculated the half-time of the wooden box from the results and the value was 10 days at the most. Of course, the box could be enclosed in another wooden box. Then the moisture movement would be decreased further. But it is probable that the half-time is never extended to 90 days.

Carboxy methyl cellulose has an exceptionally high SMR value. This must be of interest to paper conservators because this material is often used as an adhesive for paper restoration. Big difference in the EMC between the paper and carboxy methyl cellulose may cause a tension somewhere in the paper. Charcoal which is a porous material is not effective as the sorbent. The materials are also classified in Table 3 according to their SMR values in atmospheres below 30% RH. It shows clearly that Silica gel and Dydrargil are mainly used as a dehumidifier because of their high SMR values at low RH. Rice seeds tends to absorb moisture more at low RH than another materials.

TABLE 2. Classification of the material according to its SMR value

	RH < 30%	30% < RH < 70%
rice seed	+++	++
wheat seed	+	++
soy bean	++	++
rice capsules	++	++
buckwheat capsules	++	++
wheat straw	++	++
Blackwood African	+	+
Spruce	++	++
charcoal	+	+
rabbit glue	++	++
flax fabric	+	++
calfskin leather	++	++
casein	++	++
carboxy methyl cellulose	+++	++++
Dydrargil	++++	++
Silica gel RD	++++	++

+:SMR <1, ++:1 ≤ SMR < 2, +++:2 ≤ SMR < 3, ++++:3 ≤ SMR

(SMR below 30%RH is on absorption process and SMR between 30% and 70%RH is on both absorption and desorption process)

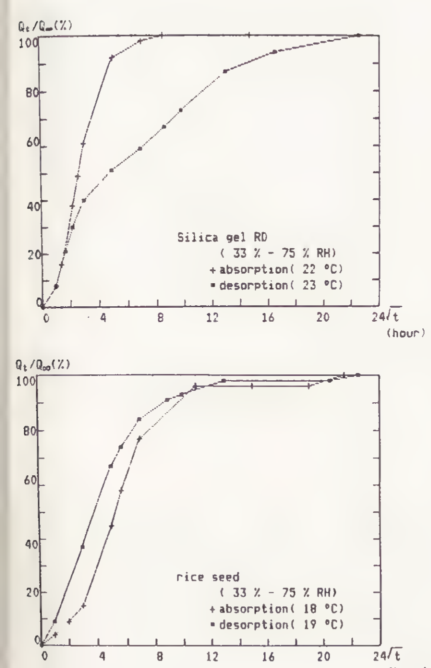

Fig.2 Absorption and desorption rates for silica gel and rice seeds.

Q_t is the amount of moisture at time t, and Q_∞ is the amount of moisture at an infinite time.

3.1. Measurement of the diffusion behaviour of moisture

Each of the materials, which was kept in about a 30% RH atmosphere produced by $MgCl_2 6H_2O$ until equilibrium was reached, was transferred very quickly to about a 70% atmosphere produced NaCl. The measurement of the weight was continued until a the material was transferred to about 30% RH atmosphere and the measurement was repeated in the same manner. To eliminate the effect of the thickness of the materials on the diffusion, the materials were spread in a 2mm layer or one particle thickness in an aluminium cup which had a 5mm diameter and which was 1cm deep. In addition, to find the effect of particle size, wheat seeds, ground wheat, and a wheat flour were prepared. The temperature changes experienced during the measurement were around 2°C.

3.2. Discussion

Figure 2 is some of the results of the measurement of the moisture behaviour in the materials. The time taken to reach 50% and 90% completion of the EMC of each material at 30% and 70% RH are listed on Table 3. Some example showed that the rate of desorption was faster than that of absorption. This was remarkable in the case of Blackwood African. This phenomenon might have happened because time spent on observation of the desorption process was too short to estimate the rate correctly. To estimate the speed of response of these materials as RH buffers, it is necessary to focus on 50% completion rather than 90%. On the absorption process the response times of rice seeds, wheat seeds, ground wheats, soy bean, Blackwood African, rabbit glue, carboxy methyl cellulose, and Dydrargil were greater than silica gel RD's and others were about much same as that. On the other hand, the response time of most of materials was smaller than silica gel's on the desorption process. Then it is possible to say that the response time of agricultural products is by no means inferior to silica gel RD. Rice seeds capsules, buckwheat capsules, and wheat straw are rather superior to that. The effect of the particle size on the moisture behaviour was shown clearly by comparing the result of wheat seeds, ground wheats, and wheat flour. The smaller the particle size, the quicker the response to the RH change.

TABLE 3. Time taken to reach 50% and 90% completion of the EMC

	absorption		desorption	
	50%	90%	50%	90%
rice seed	5.5	9.5	4	9
wheat seed	5	8.5	5.5	13
ground wheat	3	6	5	11.5
wheat flour	2.5	6	3	8
soy bean	6	13	5	10
rice capsules	2	5	4	10
buckwheat capsules	2.5	6	3	17
wheat straw	2	6	1	1.5
Blackwood African	11.5	20	4	14
Spruce	1	3.5	1.5	8
charcoal	0.5	3	1.5	2
rabbit glue	7	14	4.5	10
flax fabric	2	5.5	4	12
calfskin leather	1.5	3.5	1.5	8
casein	2	5	3	7
carboxy methyl cellulose	4.5	7	3	5
Dydrargil	4	9	4.5	9.5
Silica gel RD	2.5	4.5	5	14.5

Figures are given by square root of hours.

4.1. Measurement of RH behaviour in a showcase and deduction of SMR values

To deduce the value of the SMR from the observation of the exponential decay of RH, two experimental showcases were prepared. They were constructed from metal and glass sheet(620 x 620 x 620mm). A large thin tray for sorbents was placed just beneath the baseboard of the objects and the baseboard was finely perforated to allow air circulation between tray and display area. These two cases were placed in a humidity chamber. A hair type thermohygrograph was placed in each showcase and also in the chamber. The air leakage rate of the case without sorbents was determined as follows. First the case RH was decreased to about 40% RH and then the case was closed. Next the chamber's RH was raised to nearly 70% RH and the measurement of the change of the case RH was continued until the case RH reached about 70%. Then the rate was calculated according to the equation 1. From the preliminary experiments it became clear that mild draught within the humidity chamber had profound influence on the air leakage rate of the showcase. Therefore, the RH in the chamber was raised not by electric humidifier with fan but by means of natural evaporation of moisture using a large thin tub which was filled with water.

The RH change of the case containing natural materials were measured in the same way. After the preconditioned material which was kept at about 30% RH was placed inside the case and the case was closed, the ambient RH was increased to about 70% RH. The amount of material was 1 kg by dry weight and it corresponds to 4 kg per cubic meter of air.

Tested materials here in the showcase were rice seeds, soy bean, rabbit glue, Dydrargil, and silica gel RD. The air leakage rate of the case and the SMR value were determined by the same way as the method employed by Thomson(3).

4.2. Discussion

Table 5 gives a summary of the experimental results. From the experiment it was shown that the air leakage rate of case no.1 was 0.38 air changes per day and of no.2 was 0.35 which means about one air change every three days. The experiment showed that the SMR values calculated here were much smaller than the values derived from EMC curves. The first reason of underestimation of the SMR value is that the air within the showcase did not circulate well between the tray area and the display area. The other reason is that the air which entered the case was not dehumidified sufficiently by the material because it could not give its full SMR value. As mentioned in section 3.3 all material requires a certain period of time to reach the equilibrium, that is, it takes a certain period of time for the material to give its full SMR value. Since, the air of the showcase is exchanged totally every three days or about 70 hours, the material could not give its full value within this period of time. Therefore the effective SMR value must be smaller that the full value, and its degree is closely related to the air leakage rate of the showcase.

TABLE 4. Deduction of the SMR

showcase	material	range of RH change(%)	deduced SMR	SMR from EMC curve
1	Wheat seed	42 - 47	0.82	1.5
1	Dydrargil	39 - 58	0.36	1.5
1	Silica gel RD	25 - 52	0.48	4
2	rice seed	46 - 58	0.49	2
2	soy bean	43 - 48	0.36	1.5
2	soy bean	24 - 39	0.46	1
2	rabbit glue	43 - 60	0.42	1.5
2	rabbit glue	17 - 33	0.34	1.5

Conclusion

It is shown that the SMR value of the agricultural products is of about 1, and that their response time are by no means inferior to silica gel RD but the capsules of seeds and straw are rather superior to that. This proves that the agricultural products can be of help in controlling the climate in showcases and in small enclosed spaces. They should be used as sorbents for the reduction daily RH fluctuation owing to their low SMR values. Blackwood African showed very slow attainment of the equilibrium in the absorption and the desorption of moisture. Therefore it can be thought that this kind of wood, which is very hard, is not effective in the RH stabilization. Carboxy methyl cellulose showed an expected good result in the measurement of the EMC. The result is of interest not only to us but also to paper conservators.

As a next step, a method of conditioning these materials for museum use must be studied. It is also essential to study insecticides for these materials and to find an inorganic material to be used as a sorbent which is more stable than the agricultural products.

The relationship of the air leakage of the showcase and the SMR value of the sorbent is worth studying in greater detail. The effective SMR value seems to change its value, that is, it closely depends on the air leakage rate of the showcase. The SMR value tends to become smaller with an increasing air leakage rate of the showcase. This is thought to be caused by the intervention of the response time.

Acknowledgements

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List of materials used

Dydralgil is produced by Societ d'Exploitation du Conditionnement in France. The main component is a certain special clay.

Regular density silica gel is produced by W.R. Grace and Co., Davison Chemical Division, Baltimore, Maryland 21203, U.S.A.

NOTES

1. MIURA,S., 'Studies on the behaviour of RH within an exhibition case. Part II: The statistic and dynamic characteristics of sorbents to control the RH of a showcase',ICOM Committee for Conservation,6th Triennial Meeting,Ottawa,1981, 81/18/5

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INVESTIGATION OF SUN SHINING AT A JAPANESE HISTORICAL WOODEN BUILDING BY USE OF PHOTO-MONITORING STRIPS

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SUMMARY

It is very difficult from the conservation point of view to open works of art to the public under an environment being in contact with the open air such as temples and castles. In order to find an optimal way for conserving works of art under such an environment, the author considered to investigate first into the actual state of such an environment. So, she chose the Ninomaru hall of Nijo Castle (Kyoto city), because the hall has four sets of the outermost paper sliding doors, each set facing east, south, west and north respectively.
Although important factors for the conservation of works of art are temperature, humidity and chemical composition of their surrounding atmosphere and light, in the present paper the effect of light, especially sun light on the three sides: east, south and west sides, was investigated by using two kinds of photo-monitoring strips both of which had been developed by the author. The photo-monitoring strips are Rhodamine strips being uniformly sensitive to the visibles light and litharge strips being sensitive only to near ultraviolet light. The results obtained showed that on the east side the amount of sun light struck was the least as compared with other two, so screen paintings located in the room on the east side were kept in the best state.

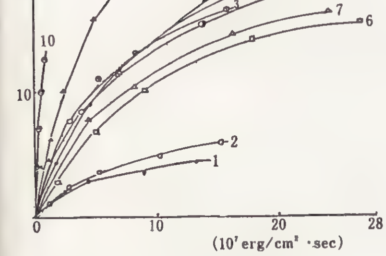


Fig.1 Color difference-accumulated irradiation energy curves of Rhodamine photo-monitoring strips

1. Introduction

It is well known that works of art can be degraded to discolor or decolor when irradiated by sun light or artificial light, that the degree of degradation depends on the wave length and the amount of light irradiated and, in general, that U.V. light can strongly degrade them. The intensity of light irradiated is usually measured by a illuminometer. However, a great many illuminometers would be required in order to measure illuminances at many places and at the same time. So, the author developed two kinds of photo-monitoring strips, Rhodamine B and litharge photo-monitoring strips. The former is approximately uniformly discolored with light of visible range and the latter discolored only with light of U.V. region.
This paper discribes the characteristics of the two photo-monitoring strips and their application for the actual measurements at many locations in a Japanese historical wooden building.

2. Preparation and characteristics of photo-monitoring strips

2.1 Preparation of photo-monitoring strips

Filter paper (Tōyō Roshi No.5 for qualitative analysis) are immersed in a 1% ethanolic solution of Rhodamine B (C.I. No. 45170), removed from the solution, blotted off an extra solution and dried in the air in the dark. After drying, the paper are cut to form 2cm x 2cm square strips. We call them Rhodamine B photo-monitoring strips.
Litharge, being specially chemical pure grade (produced by Wakō Junyaku Co.), is slurried with a 10% aqueous solution of glue and the slurry thus obtained is applied to a paper board, dried in the litharge photo-monitoring strips.
The two kinds of photo-monitoring strips thus obtained are both stored in a dark place.

2.2 Characteristics of photo-monitoring strips

Photo-monitoring strips were irradiated by monochromatic lights by using Model CRM-FA grating type irradiation spectroscope (produced by Nihon Bunko Co.). Monochromatic lights used had wave lengths, 699, 647, 596, 544, 498, 441, 390, 284, and 235nm respectively. Discoloration of the strips was measured in terms of the color difference (ΔE) from the original by using a color computer (produced by Suga Shikenki Co.).
Color difference-accumulated irradiation energy curves obtained are shown in Figs.1 and 2.

The accumulated irradiation energy required for the color difference, ΔE, being equal to 5 at which the strips can be barely recognized to have faintly discolored by the naked eyes can be obtained from Figs.1 and 2.
Rhodamine B photo-monitoring strips exhibit similar color difference-irradiation energy curve in the range of wave length between 338 and 598nm and that they are very sensitive to light below 338nm but stable against the light above 598nm. On the other hand, litharge photo-monitoring strips are sensitive only to light below 441nm and fairly stable against the light above 441nm.
These facts tell us that Rhodamine B strips can be used for monitoring visible light as well as U.V. light and litharge strips for only U.V. light. Lights used for illuminating works of art, both sun and artificial lights, contains U.V. and visible lights, although their proportion is different from one light source to others. Therefore the use of both Rhodamine B and litharge strips is believed valuable for monitoring the light to illuminate works of art.

These photo-monitoring strips showed ΔE with mean errors below 10% in the range of wave length between 284 and 596nm, including most of U.V. and visible region of sun lights striking on the earth. So, it is believed that these photo-monitoring strips can be an inexpensive simple and easy to use tools for monitoring lights illuminating works of art.

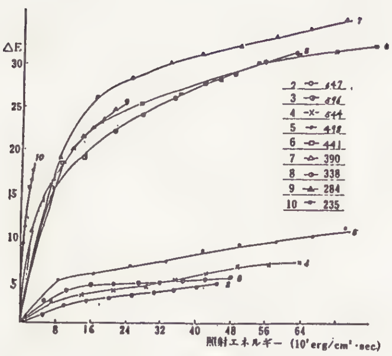


Fig.2 Color difference-accumulated irradiation energy curves of litherge photo-monitoring strips

Figs.1,2
1 ▬ 699, 2 –○– 647, 3 –⊙– 596
4 –×– 544, 5 –●– 498, 6 –□– 441
7 –△– 390, 8 –◐– 338, 9 –▲– 284
10 –⊖– 235

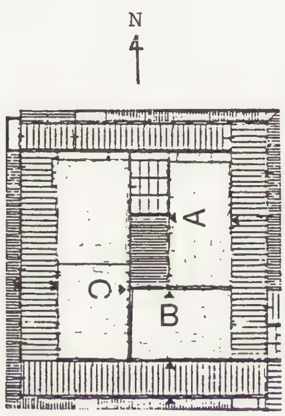


Fig.3 A, East side
B, South side
C, West side

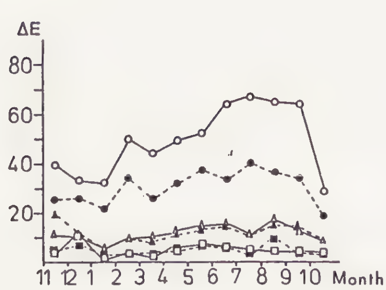


Fig.4 X=Rhodamine B, Y=east

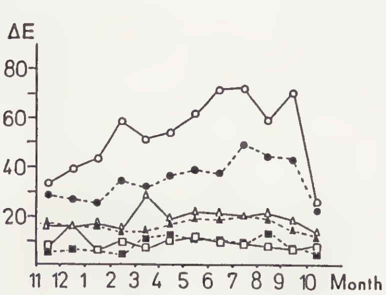


Fig.5 X=Rhodamine B, Y=west

3. Application of photo-monitoring strips for monitoring sun shining at a Japanese historical wooden building, Nijo Castle, Kyoto

Nijo Castle, a typical Japanese historical wooden building, was built at the beginning of the seventeenth century in Kyoto by Ieyasu Tokugawa, the first shogun of the Tokugawa shogunate, as his official residence there. The ōhiroma (a hall) of Ninomaru Palace, one of the building within the ground of Nijo Castle, was chosen as the object to be investigated for the sun shining. As shown in its plan view (Fig.3), the ōhiroma is a square having four sets of outermost paper sliding doors, each set facing east south, west and north respectively. As shown in Fig.3, the ōhiroma surrounded by the four sets of doors consists of four main rooms and closet room surrounded by the four rooms. These main rooms are further surrounded by four sets of corridors. It has also long eaves enough to prevent from directly raining and sun shining into the rooms. It is also famous for its paintings on the sliding screens forming innermost boundaries of four individual main rooms. A great many peoples always visit there to see these paintings. These paintings are illuminated indirectly only by sunlight due to being prevented from its direct effect by the long eaves, wide corridors, paper sliding doors and room width. Among paintings in three rooms A (east), B (south) and C (west) in Fig.3 the paintings in the east room (A) are kept best in color, showing the least deterioration.

So, the attempt was made to measure the degree of the effect of sun shining on the three sides: east, south and west, by using Rhodamine B and litharge monitoring strips placed at various spots as shown in Fig.3. Strips are left at each spot for seven successive days each time and then measured for ΔE by the color computor previously mentioned. The monitoring was done once every month over the period from November 1985 to October 1986.

ΔE values of Rhodamine B strips thus obtained at various spots on the east, south and west sides are shown in Figs.4,5 and 6 respectively. Similar ΔE values of litharge strips on the three sides are also shown in Figs.7,8 and 9 respectively. Figs.4-9 generally show that the effect of sun shining gradually attenuates from the outermost spots, the outside of the paper sliding doors, through the inside of the doors and then the inner edges of the corridors and to the innermost spots of the rooms on all the three sides.

Rhodamine B strips generally show ΔE values greater than those of litharge strips at the same spots and especially at the outermost spots they show ΔE values about twice to thrice those of litharge strips. E values of Rhodamine B strips at a set of four spots on a given side, for example, on the east side, namely ΔE values at the outside and inside of the paper sliding door, the inner edge of the corridor and the innermost spot of the room, significantly decrease in this order. Those of litharge strips at the four spots also show a similar but less significant decrease. Therefore, it can be said that Rhodamine B strips are more suitable than litharge strips in such an application as in the present study.

From Figs.4-6, ΔE values at the outside of the doors are high between June and September, and low between October and January. However, ΔE values at the innermost spots of the rooms do not show such significant difference. Therefore, the innermost spots of the main rooms, namely the places where paintings are located are effectively protected from the direct sun shining.

In order to compare the long lasting effect of the sun shining on the three different sides of the ōhiroma, annually mean ΔE values were obtained from Figs.4-6 as shown in Table I.

Table I shows that the innermost spot of the east room (A) where screen paintings are present is lowest in ΔE values among all the innermost spots of the three rooms (A,B and C). This clearly explains the fact that screen paintings in the east room are best kept. Table I also shows that the screen paintings in the room A are effectively protected from the sun shining because of their receiving only 10.8% of the sun light.

4. Conclusion

For the purpose to check in a easy and simple way the effct of the illumination on works of art, two kinds of photo-monitoring strips, Rhodamine B and litharge monitoring strips, were developed. The former is almost constantly affected by lights having wave lengths from 338nm to 598nm and the latter is sensitive only to lights having the wave length below 441nm.

The two photo-monitoring strips were applied to check the effect of sun shining at various spots in a typical Japanese historical wooden building, Nijo Castle, Kyoto over a year.

The results obtained showed that Rhodamine B photo-monitoring strips are more suitable than litharge photo-monitoring strips,

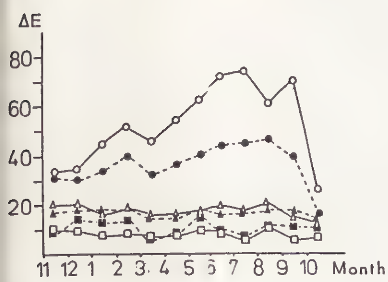


Fig.6 X=Rhodamine B, Y=south

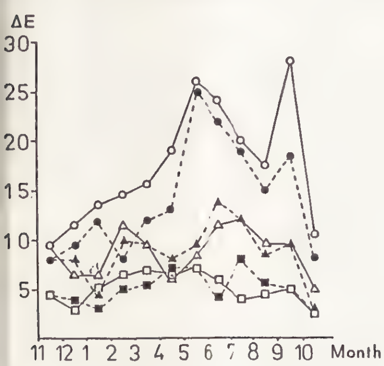


Fig.7 X=litharge, Y=east

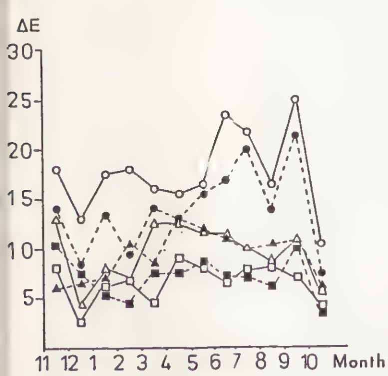


Fig.8 X=litherge, Y=west

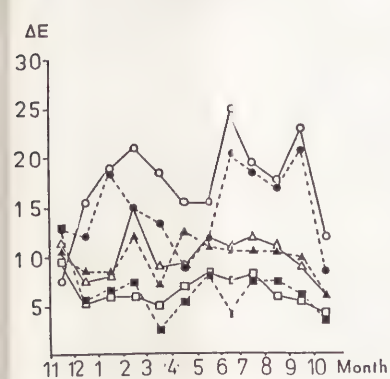


Fig.9 X=litherge, Y=south

Figs.4-9 E Values of X strips exposed every month at various spots in the ōhiroma on the Y side

- ○, outside of the sliding door
- ●, inside of the sliding door
- △, upper outermost part of the room A(B,C)
- ▲, lower outermost part of the room A(B,C)
- □, upper innermost part of the room A(B,C)
- ■, lower innermost part of the room A(B,C)

that the screen paintings located at the innermost of the room on the east side are most effectively protected from sun shining among all the screen paintings in ōhiroma of Ninomaru Palace and that the effect of sun shining on the east screen paintings is only 10.8% of that at the outside of the paper sliding doors.

Table I

Annual mean ΔE value of Rhodamine B strips at various spots in ōhiroma of Ninomaru Palace

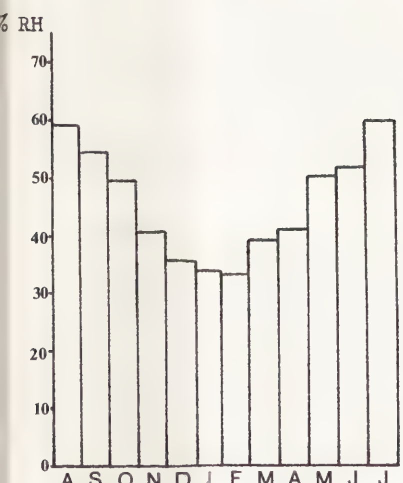
Side	location		annual mean ΔE	degree of mitigation*,%
East	outside of the door		50.0	100
	inside of the door		31.4	62.9
	inner edge of the corridor	upper	11.9	23 8
		lower	12.3	24.5
	innermost spot of the room	uper	5.4	10.8
		lower	5.4	10.8
South	outside of the door		52.4	100
	inside of the door		36.0	69.0
	inner edge of the corridor	upper	17.0	32.7
		lower	16.1	30.9
	innermost spot of the room	uper	7.6	14.7
		lower	10.3	19.7
West	outside of the door		53.7	100
	inside of the door		35.5	66.1
	inner edge of the corridor	upper	18.8	35.0
		lower	14.5	26.9
	innermost spot of the room	upper	9.3	17.3
		lower	8.8	16.3

$$\text{* degree of mitigation} = \frac{\Delta E \text{ at a spot of interest}}{\Delta E \text{ at the outside of the door}} \times 100$$

SUMMARY

A system of plumbed-in humidifiers in Huntly House Museum is assessed. The benefits in improved environmental conditions are demonstrated. Everyday practical problems of machine design, plumbing, control, mechanical maintenance and cleaning are discussed and some solutions are offered.

The system has been shown to be useful, but requires great attention to detail to be safe and effective.



Monthly averages R.H.
August 1976 - July 1977

Before humidification

Fig. 1

SOME PRACTICAL PROBLEMS IN RUNNING A HUMIDIFICATION SYSTEM IN HUNTLY HOUSE EDINBURGH

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Introduction

Huntly House is a 16th century building, much extended and subdivided down the centuries, consisting of a series of small rooms linked by narrow spiral staircases. It is mainly on three floors, but the floor level changes on both the first and second floors with short flights of steps linking many of the rooms. The result is a building historically and architecturally interesting, but awkward and inconvenient in many ways as a museum.

In winter the building is heated by a series of small, fan-assisted, convection heaters in each room, and generally low relative humidity levels were recorded. This problem was first identified and studied by my forerunner as Conservation Officer, Mr David Watkinson (now at Department of Archaeology, University College, Cardiff).

Environmental Conditions

Monitoring of R.H. levels has been done over a number of years in two main ways. Three thermohydrographs were placed in selected locations to monitor the daily and seasonal variations in R.H., and spot testing with a whirling hygrometer was carried out daily in every room to check for variations in different parts of the building. A block graph (fig. 1) compiled from monthly averages of R.H. readings illustrates the extent of the problem. Summer R.H. levels when the heating is off are generally 50-60% with some variation according to weather. Winter R.H. levels varied from 30-40%.

This presented particularly obvious problems in a series of rooms on the first floor which have wood-panelled walls, where splitting of the panelling has occurred in the past. It also threatened many objects in the collections of mixed local history and applied arts exhibits, in which all materials, organic and inorganic, are represented.

Air conditioning was not a technically feasible solution, because of the complicated structure of the building and its historical and architectural importance, which precluded running the necessary ducting through the rooms. It was therefore decided to try installing a series of humidifiers, and Mr Watkinson had already purchased two humidifiers as a trial when I took up my post in 1976.

The Humidification System

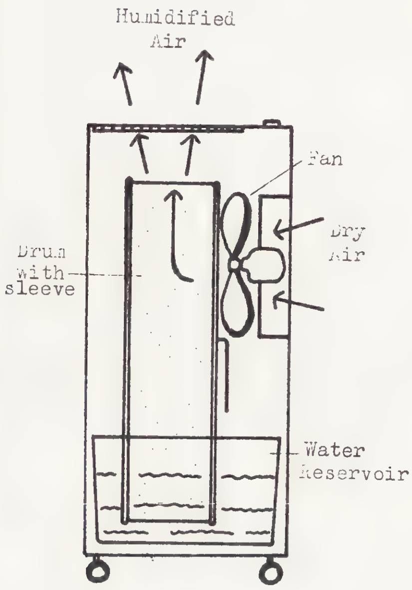
The humidifier selected was the Gibson Century Air Humidifier (1). This is a cheap and simple fan-ventilated drum evaporator and quite small and compact which was essential to fit into the small and awkwardly-shaped rooms (fig. 2). Trials with the first two humidifiers showed they could humidify a small room to reasonable levels (50-55% R.H.). It was therefore decided to humidify all rooms in the museum. Some sections of the displays did not strictly need high humidity levels, but most displays are mixed materials and we wanted to retain flexibility to change them around. I decided it was best to have a stable environment all year round rather than a fluctuating one, even if the absolute level of stability was a little high for some objects. Individual controls on every humidifier enable selected humidifiers to be shut off to suit exhibition purposes without affecting the rest of the system.

Monitoring of the effectiveness of the system has shown that although there are still small daily and seasonal fluctuations these have been significantly reduced (fig. 3).

Hand-filling of the machines was deemed impractical, and it was decided they should be fully plumbed-in. Eventually 22 humidifiers were installed and plumbed in throughout

the building in 1978-79. The plumbing is by narrow pipe with a slow feed, and an individual stop-valve is fitted outside each machine. The system is supplied with ordinary domestic tapwater of drinking standard.

The humidistat controls on the Gibson Century, which are part of the machine, are crudely marked in notches not precentages, so determining the level at which they should be run was a matter of trial and error. After careful monitoring a satisfactory level was discovered. The humidifiers are run year-round, running at a low level in summer which helps to even out the variability of the weather.



Gibson Century Air Humidifier

Fig. 2

Technical Data

Evaporating Capacity: up to 2.2 litres/hr
Room Capacity: up to 430m^3
Power Consumption: 50 watts
Dry Weight: 21.3 kg
Water Reservoir Capacity: 45.46 litres
Power Supply: 220/240 V., 50 HZ
Fan Motor: High 1050 rpm
Low 600 rpm
Dimensions: 660mm x 610mm x 305 mm

Problems

My office and laboratory are in another building, so daily supervision has to be carried out by the attendant staff. Regular notices are issued to them to tell them what the setting should be. The control knobs are sited on the top of each humidifier, and were soon found to be irresistible to visitors, so perspex covers were purchased to reduce tampering. The attendants were also warned to check the controls regularly on their patrols to ensure they had not been altered.

After about two years I discovered that on hot summer days the controls were sometimes set unaccountably high. It turned out that some new attendants who did not understand the system had found that the humidifiers produced a comfortable cooling effect at high levels. Training the attendant staff had to be given a new priority, and I now find it essential to explain the system at least once a year, particularly when there are staff changes. This is time consuming but useful. We could not run the system without the co-operation of the attendants, and regular contact with them increases their involvement and commitment to keeping the system functioning.

Maintenance

More serious problems have arisen with maintenance. The humidifiers are serviced annually. The fans and motors are checked and lubricated, and worn bearings and grommets replaced, but the service engineers frequently have to be recalled to deal with problems. Some problems arise from the plumbing (air-locks or valve failures resulting in the failure of the machines to fill). Others are faults with the machines themselves. The simple ball-valves which should control the filling can fail, which may lead to overflow of the machines. Given the slow feed of water this does not usually result in large floods, and this is normally quickly spotted. The heating system is put off at night, and R.H. rises accordingly, so the humidistats normally shut off the humidifiers at night. Since they are not running at night they don't fill either, and overflow is most common during the day when it can be quickly seen, and the valve on the infill pipe can be closed. Overnight leaking on one occasion did, however, result in a large pool of water.
At the time of writing it has been suggested to me that this danger could be reduced by placing the humidifiers in a flat tray. These problems would not occur in a system which was not plumbed and not continuously fed.

The bearings on which the drum is located are also very simple. They can wear or break which causes the drum to revolve unevenly with a grinding noise, or stop. The bearings then have to be replaced. This can be exacerbated by careless handling of the drum when it is removed for cleaning, but also happens from ordinary wear on the bearings. Occasional faults also develop in the motors. On average the engineers have to be called every five or six months to deal with three or four humidifiers. Although most faults are minor it is expensive and time consuming to get repairs done, and of course it leads to fluctuations in the relative humidity which the system was originally installed to prevent.

After about eight years use one humidifier is said to be beyond repair. I do not know what the life-span of the other machines will be, but I had taken little account of maintenance and replacement costs when the system was installed. Clearly any museum considering installing such a system should add to their capital costs a substantial margin for maintenance and replacement, perhaps 15%.

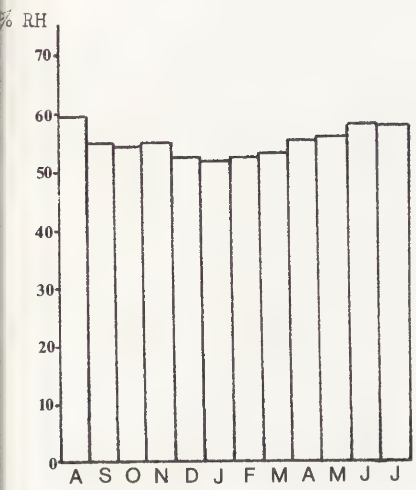
Cleaning

The most serious problems have arisen with cleaning. Initially I took no account of this, and we only cleaned machines occasionally, usually when they had a fault or looked visibly dirty. In 1981 we called in Environmental Health Officers to do a check as a precaution. Their report was shocking. There were unacceptably high levels of bacteriological content in the water of the humidifiers, and this was considered a potential health risk to both staff and public. We were advised to take immediate action or to stop running the system.

All the humidifiers were thoroughly cleaned, and a rigorous cleaning programme was instituted. Every humidifier is cleaned once a month (for convenience they are cleaned on a rota basis, one or two being done each morning). To ensure regular cleaning each humidifier was numbered and a register was begun. When a humidifier is cleaned the register is signed by the attendant who cleaned it, and any relevant comment added. The register is periodically checked by myself, and is open to inspection by Environmental Health Officers.

For cleaning the humidifier is drained fully and washed out with a disinfectant solution before refilling. The belt is removed and washed out before being replaced. "Micropur" water purification tablets (2) are added to the water between cleaning sessions. It takes an average 30 minutes to drain, clean and re-instate one humidifier, which means a considerable investment in staff time for a small institution.

Occasional checks are now carried out on the water by Environmental Health officials at our request. The rigorous cleaning programme seems to have solved the problem, and on the most recent check all samples were satisfactory and no health risks were identified. Nevertheless it is essential not to let the cleaning programme lapse, and this does present problems when staff time is under great pressure.



Monthly averages R.H.
August 1979 - July 1980

After humidification

Fig. 3

Conclusion

The system has proved useful, and regular monitoring has shown reasonable R.H. levels for most of the year, though without total stability of environment. However it does require constant attention to keep the machines functional, clean and at an appropriate setting. It has been important to educate the attendant staff regularly about the reasons for environmental controls, and requires a high level of co-operation from them without which it would be impossible for the system to operate. Running costs have been higher than anticipated because of the amount of maintenance required, and replacement costs will be an increasing problem as the machines age. It is a useful system, but it is not a simple solution to a problem.

Notes

1. Gibson Century Air Humidifier, supplied by Beta-Plus Ltd., 177 Haydons Road, London SW19 8TB.
2. "Micropur" tablets, supplied by Fecon Ltd., Fecon House, Garth Road, Morden, Surrey.

SUMMARY:

Wooden churches are common in Norway. Very many of these churches are poorly insulated or not insulated at all. On account of the cold winters this leads to great seasonal variations in indoor climate, with extremely dry air in the winter. This has disastrous consequences for church inventory: the woodwork cracks and the paint peels off.

Five mediæval wooden churches are being examined in detail with respect to climate by means of advanced computing equipment. RH and temperature are being measured outside and inside, at floor level, just under the roof and by selected objects. At the same time measurements are being made of changes in dimension in the same objects.

The purpose is to understand the total climate, the local climates and the response time of the wood in relation to the climatic changes, so that practical measures can be implemented to improve conditions for building and inventory.

ADVANCED MEASURING OF THE CLIMATIC CONDITIONS IN THE MEDIÆVAL WOODEN CHURCHES IN NORWAY

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THE WOODEN CHURCHES - HOW WERE THEY ABLE TO SURVIVE

Of originally roughly 1000 mediæval wooden churches, the stave churches as they are called, only 32 are left in Norway today. These churches were built in stave construction, a post/girder technique, in which the outer walls are formed of standing planks or boards dovetailed into a supporting frame. This method of construction had become very highly developed with carefully considered details. The reason that these churches are still standing with their original timber is undoubtedly the result of this successful method of building and of continual maintenance over a period of 800 years with the churches being tarred every three years.

Nevertheless, the continued existence of these churches is threatened by a number of external factors. The foundation structures must be continually checked to prevent damage from rot caused by damp ground. Three churches standing in a region where the long-horned beetle **Hylotrupes bajulus** is prevalent have been safeguarded against attack by such insects through fumigation and spraying with insecticides. Systematic maintenance is necessary to protect these churches from other damage caused by the tough Norwegian climate.

THE CLIMATE - BEFORE AND NOW

The churches were of course originally unheated, but in this century central heating has become quite common, and since electricity is cheap in Norway, many churches have been heated like private homes every single day during the winter period. The consequences of these new climatic conditions were not understood until much later - and many users of the churches have not understood these facts yet. They cannot see that intensive all-year use of 2/3 of the churches means that the indoor climate is subjecting the buildings and their inventory to great strain and damage.

Luckily 12 of the stave churches are still unheated, being in use only in the summer season, while 20 are in use as ordinary parish churches and are heated electrically in the cold part of the year.

The unheated churches have an indoor climate that is roughly the same as the climate outside. The delayed reaction to climatic change which one sees in stone buildings does not occur in wooden buildings. Their structure can only absorb dampness to a moderate degree and has in addition too little heat capacity to be able to act as an effective buffer between indoor and outdoor climate.

"MODERN" CLIMATE - NEW CONDITIONS

The parish churches are in use for large parts of the week, not only for services but also for other purposes connected with parish activity. In the cold season, which can be as long as 8 months, churches are in most cases continuously heated. Modern demands for comfort mean that the indoor temperature is at certain periods around $+20^{o}C$, while the temperature outside may often drop to $-30^{o}C$.

With temperature differences of up to $50^{o}C$ between indoors and outdoors, and with an 8 cm thick external wooden walls, often with gaps between the boarding, it is obvious that energy consumption is enormous.

The draughty walls also lead to great changes of air. Cold air is sucked in from outside, heated up and released again through gaps in the upper part of the church room.

"DRIER THAN THE SAHARA"

This of course has enormous consequences for the indoor climate: it is a well known fact that the amount of water air can absorb varies greatly with temperature. At $-30^{o}C$ the maximum amount of water air can contain is under 0.8 g water per kg air, while at $+20^{o}C$ it can contain 14.7 g per kg air. When air with a temper-

ature of -30°C is heated to +20°C, there is a radical reduction of the relative humidity (RH), i.e. the relationship between the amount of water the air in fact contains, and the maximum amount of water that can be absorbed. If the outside air has 90% RH, this air will have only 6% RH after being heated to +20°C.

This results in the air, since it is so dry, absorbing moisture from the surroundings. Wood is a hygroscopic material, and the moisture content of the wood varies with the RH of the air, a relationship that is expressed in terms of the equilibrium moisture content of the wood. Dry air will absorb moisture from the wood. The enormous change of air that we can observe in these churches further increases this drying-out process.

Changes in the equilibrium moisture content of wood lead to shrinking or swelling. How great these dimensional changes may be depends to a large extent on the kind of wood. Pine, **Pinus sylvestris**, which is the only building material used in the mediæval churches in Norway, shrinks and swells easily. The tangential shrinking is nearly twice as great as the radial shrinking, which necessarily leads to cracks appearing in the material.

THE BUILDINGS ARE SUFFERING

What happens to these churches when the inside air is so dry? In the structure of these churches the damage we find is first and foremost in the form of cracks. Such damage is of course also found in unheated churches, but then it is limited and slight and can as a rule be traced back to defective material. The fact that there is especially little damage of this type is the result of meticulous selection of the material, timber that was furthermore specially treated before felling to prevent cracking.

In the outer walls of a heated church the vertical planks will shrink further and cause even more cracks in the wall. We have observed 10-15 mm cracks in some wall planks, but fortunately none of these cracks went right through. The wall becomes leaky in the joint between two planks or in the transition from plank to frame.

In the heated churches we can also see that the massive, free-standing posts, which can be up to 12 m high, have developed large cracks. These cracks can be 40-50 mm wide, 150 mm deep and nearly 3 m long. This damage does not represent structural weakening of the posts as these are statically greatly oversized. Visually, however, the damage is considerable.

THE INVENTORY IS BEING DAMAGED

Some of the stave churches have polychrome mediæval inventary such as crucifixes, statues of saints and triptychs. These objects have wood, mainly pine, **Pinus sylvestris**, and oak, **Quercus spp**, as their basic material, and this is of course subject to the climatic strains previously described. These strains lead to splitting of the wood and flaking of the polychromy.

The state of preservation and conservation varies for these objects, and systematic registration has therefore been undertaken of all polychrome mediæval inventory to be found in the Norwegian churches. Altogether this means a total of 236 objects distributed between 96 stone churches and 88 wooden churches, including 17 stave churches.

The report on the state of the good 60 objects that need treatment was sent to an art historian who produced a list in order of priority based on the criteria **age**, **rarity** and **state of preservation.**

Unfortunately, however, we see that when the objects are sent back to their churches after conservation and restoration at our studio in Oslo, new damage occurs. This is damage we believe to be caused by the climate in which they are again placed.

The hygroscopic basic material swells and shrinks according to the relative humidity of the air. The gesso ground layer, which consists of chalk powdered in animal glue, loses its elasticity and ability to adhere in a dry environment, and it swells in damp surroundings. The paint layer, having lost its elasticity, cannot follow the movements of the underlying layers. Tensions arise in the stratigraphy and finally these layers, which are so important to the work of art, fall off.

NATURAL CLIMATE VERSUS ARTIFICIAL CLIMATE

Let us take a closer look at the relationship between state of preservation and climate, using stave churches with mediæval inventory as a starting point. Among the 17 relevant stave churches we find a group of churches with a "natural" climate, which is approximately identical with the conditions in which the objects were originally meant to be kept, and a group of churches with an "artificial" climate, a far cry from both a "natural" climate and an "ideal climate", in which temperature and relative humidity are kept more or less constant.

The "natural" indoor climate fluctuates a good deal in the course of the year. In Urnes we have recorded temperatures which in the winter fall far below zero and in the summer rise to +20°C. The relative humidity varies between 30 and 93%. Nevertheless, this is not so bad as it may seem: because the intervals with dry air (30-45% RH) are very short (hours only), the wood apparently does not react until RH increases again.

On the other hand, in the heated churches, such as Ringebu, one can note RH of 5 to 30% in the winter months. When RH lies in this area over a lengthy period, the wood will react by giving off moisture to the surroundings and thus dry out. The variations in a summer month without heating lie between 40 and 60%, which as far as we can judge does not lead to the wood drying out.

The table below shows the relationship between the climate and the state of preservation of the 30 mediæval objects, some of which have previously been repainted while others have not.

	churches	mediæval objects	objects that need treatment
unheated churches	8	11	3[1)]
heated churches	9	19	12[2)]

1) 1 object restored after 1960. Damage due to overpaint.
2) 7 objects restored after 1960.

In the heated churches 12 of 19 objects need treatment, while only 2 out of 10 must be restored in the unheated ones. If we disregard the bearing of earlier restoration, handling, washing, etc. on present restoration needs, we can thus say that the chance of an object needing treatment is approximately 3 times greater in a heated stave church than in a stave church with a natural climate.

As not one of these churches has anything even like a "so-called" ideal climate, we do not know what the relationship would have been between the state of conservation in churches with a natural climate and the state of conservation in churches with an ideal climate.

We must also make certain reservations concerning groups of objects painted in other techniques than the traditional method of the Middle Ages with glue-soaked wood with canvas-reinforced chalk-glue ground, and with painting structures mainly based on pigments powdered in drying oils, or with distempers on wood. For the time being we have thus chosen to concentrate on mediæval objects in mediæval churches where the variable is the indoor climate, and we have tried to quantify the relationship between climate and state of conservation. Even now the tendencies seem clear: <u>there can be no doubt that an uncontrolled, artificial climate is far more harmful than a natural climate</u>.

We must therefore do something about the climate in the heated churches to prevent newly treated objects from being ruined as soon as they are returned to their churches. Until this phenomenon, which may be designated the **Sisyphus syndrome**, is reduced to a minimal factor, it may seem pointless to treat objects at all - except to give them surface protection.

Many conservationists who are experts in this field believe that the ideal climate for works of art on wood is +18-20°C with an RH of 55% +/-5%, but that a variation of between 45 and 65% RH over the year is acceptable. These are conditions that it is difficult to achieve in the churches. The church is God's house in which the priest and congregation gather together for religious purposes and not primarily to look at church art. They want the building to be reasonably warm in the winter. The same goes for the organist who wants the chance to practise and who perhaps looks upon the church as essentially his place of work. Yet when

Fig. 1:
This photograph shows the Madonna from Hedalen stave church taken 10 years after the last restoration. In the course of this time the sculpture has lost approx. 17 cm^2 of its original polychromy. The cause of this peeling is the unstable climate.

Photo: S.A. Wiik 1980

these demands for comfort are met, the air gets so dry that the church art illustrating the word of God will be ruined.

SHOWCASES

A good climate for these objects can perhaps be achieved by the use of showcases. In some instances this is not a practical possibility, in other cases it is not compatible with the demands made by the liturgy. In contrast to other regions such as South America, there is no tradition in Norway of using showcases in churches. The Central Office of Historic Monuments has therefore not entered into a discussion of the realities with the parishes on this question. It is nevertheless possible that as a result of the knowledge we gain through this project we must revise our attitudes to the use of showcases.

HUMIDIFIERS

Why can we not solve the climate problem by installing humidifiers in the churches? If one increases RH to 55% with an indoor temperature of +20°C, the climate will be good for both congregation and objects.

However, vapour pressure in the air will be high, approx. 10 mm Hg. There is no vapour barrier on the inside of the outer walls. Gradually as the air finds its way out through the wall, the temperature will fall and at some point the air will reach its saturation pressure and condense. With the values mentioned in the example above, condensation will occur at +11°C. This will lead to dampness in the wall structure with the danger of ice formation and frost damage in cold periods, and the danger of damage from rot at more moderate temperatures.

We can see the frightening consequences of the use of humidifiers in a nearly 100-year old church built with a wooden-framework structure comparable with stave technique. The church has been insulated with mineral wool. Indoor heating and humidifying have been set at +20°C and 50% RH. Even after a short time large amounts of dampness were found in the timber. The visible surface damage is extensive peeling of the paint and severe swelling of the panelling.

If one humidifies the indoor air, the only way of protecting the structure of the walls, floor and roof against damp is to place a 100% impermeable vapour barrier on the inside of the structure. In theory this is technically possible, but in practice defects and damage will easily arise and cause the barrier to leak. In a stave church, where the structure is in addition fully exposed to view, both architectonic and antiquarian considerations make the use of vapour barriers impossible.

Thus humidifying is no solution either.

THE CONFLICT: USER - BUILDING - ART

In other words we have at least three parameters to take into account: the <u>church user's</u> desire for comfort (the priest wishes to use the church as often as possible, he wants as many people as possible to come as often as possible, the organist wants a chance to practise and then both he and the organ need to be warm, he feels), the <u>church building</u> which cannot stand up to our using humidifiers with the necessary capacity for RH to reach an acceptable level for the works of art, and the <u>church art</u>, which can well stand the cold if only RH is stable and high enough.

Three parameters on a collision course.

MONITORING THE CLIMATE AND ITS EFFECT ON WOOD

It is therefore necessary to find other methods of solving the problem of mediæval objects drying out in our stave churches. To be able to evaluate alternative measures it is necessary to study the climate inside these stave churches in detail.

We have therefore chosen 5 stave churches with mediæval inventory in order to undertake more detailed investigation of the local climatic conditions inside and outside these churches. Three churches, Ringebu, Hedalen and Kaupanger are heated parish churches, while two, Urnes and Hopperstad, are unheated and in use as church museums.

Since September 1986 conditions have been recorded electronically and data are transmitted to a computer for further processing with special programmes for indoor climate regulation. We have chosen to measure the following climatic factors:

1. Air temperature and relative humidity outside.
2. Air temperature and relative humidity inside at floor and roof.
3. Air temperature and relative humidity inside at east and west ends.
4. Air temperature and relative humidity in the immediate vicinity of particularly important objects.
5. Dimensional changes (shrinking and swelling) in the woodwork of especially important objects.
6. Electrical power and consumption in the church.

Fig. 2:
Hedalen stave church one day in March. 8 cm thick walls separate the congregation and church inventory from the severe Norwegian winter. The difference between inside and outside temperature can be as much as 50°C.

Photo: J.C. Eldal 1971

For recording temperature and relative humidity in the air a combined electronic sensor is used. Calibration of the RH meter takes place electronically through changes in the computer programme. This reduces the risk of damaging the instrument. To measure the small dimensional changes in the woodwork we have had a sensor designed which can measure changes down to approx. 1/100 mm. In breadth and thickness the instrument measures 10 x 8 mm. Its length is tailored to the relevant measurement point. All values are automatically converted into ratios so that different measurement points in a church can easily be compared. The computer programme compensates for any expansion of the instrument due to temperature.

In order that a picture can be formed of how the churches are heated, equipment has been installed that measures the electrical power being used at any time in the church. These data can also be obtained in the form of accumulated values so that one can evaluate daily or weekly consumption of electricity.

In the church or in a nearby building a computer has been installed, and every ten minutes it collects information from the various sensors inside and outside the church. All information provided by one sensor can in this way be precisely related to information provided by another sensor at the same point in time. The computer has the capacity to store data for up to 48 hours.

Every 24 hours data from all 5 churches are automatically transmitted over the ordinary telephone network to a central computer at the research institution SINTEF (Foundation for Scientific and Industrial Research) in Trondheim, a distance of 300-400 km. This central computer stores the information for further processing.

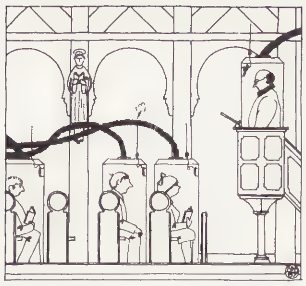
What happens in fact to the enormous volume of data collected? It is important to approach the task from angles that make it possible to filter out all irrelevant data so that only that information which is relevant to the harmful effect of the climate is left.

In the course of further processing, data from different measurement points can be contrasted and compared. Real time recording in the churches makes it possible to read off the response time between changes in RH and the shrinking and swelling of the wood, to evaluate the relationship between indoor and outdoor climate in relevant periods, and to compare local climatic variations inside the church.

Through this kind of stepwise processing of the volume of data, in which each operation only treats a sorted part of the information, one can form a picture of the causes and effects behind the damage done to the wooden objects.

Standard programme packages for computer processing of climatic data make it possible to carry out statistical analyses of the material with a view to searching for special characteristics in the mass of data, such as changes in the dimensions of the wood. By hunting backwards through the mass of data for climatic causes of these dimensional changes, one has a good angle from which to approach an evaluation of the connection between indoor climate and damage to building and inventory.

Even now we can see a number of climatic factors that seem surprising in relation to what we had imagined when we started. Among other things the local climatic variations between different places in a church are far greater, both when it comes to average values and variations over time, than we had hitherto been able to determine by means of conventional thermo-hygrographs. In addition we have been able to record lower RH than we had hitherto thought possible, particularly in Ringebu church where the lowest value so far has been 5.7% in the upper part of the nave.



The final solution?

The next step will then be a study of what measures can be implemented to improve climatic conditions so that damage to buildings, objects and decoration can be reduced to a minimum. Measurements should be made for at least one, but preferably two years. So far we have deliberately avoided entering into a discussion about practical measures at this time, so that our starting point is as unprejudiced as possible when we have done an analysis of climatic causes and effects. At the present time, we feel that these problems might be solved not by inventing a new and miraculous solution, but by applying a combination of small measures in order to satisfy the demands made by the church user without damage to church buildings or church art.

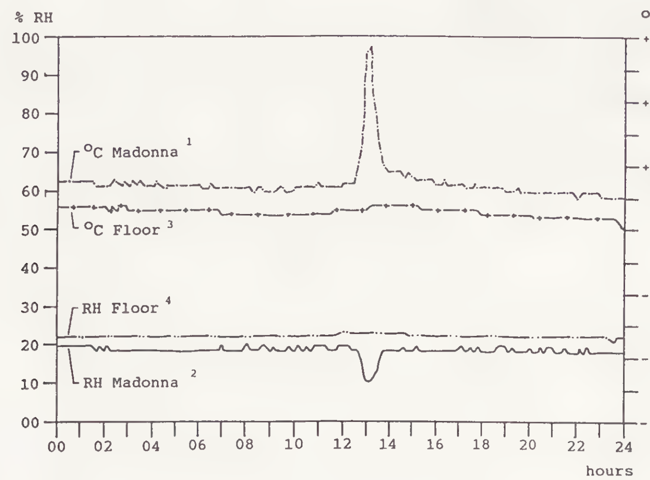


Fig. 3:
This diagram shows the great variations in local climate in Hedalen stave church on 18 January 1987, when the outdoor temperature was between -14 and -20°C, and RH swung between 65 and 80%.

Graphs 1 and 2 show how the temperature rose almost 20°C in the course of barely one hour, and that as a result of this RH dropped by almost 10%. The changes were due to the fact that for this short time in the middle of the day the low-altitude winter sun struck the north wall of the nave of the church precisely where the Madonna had been standing. Is it these brief variations in RH for just a few months in the winter that have done the enormous damage to the sculpture (Fig. 1), or are the changes too fast for the wood to react?

Graphs 3 and 4 show the stable climate down by the floor just a few metres farther away. The sun has no influence, the temperature is in principle 3°C lower and RH is stable and 2-3% higher.

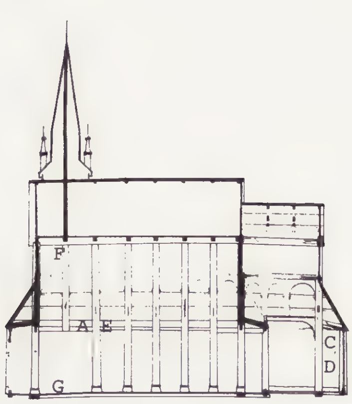
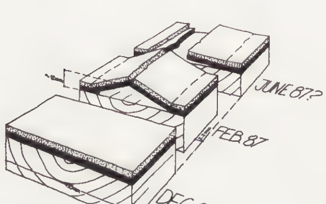


Fig. 4:

KAUPANGER CHURCH on 04.02.87 at 09.31

	Temp.	Humidity	Changes in dimension
A. Outside N	4.2°C	88.9%	
B. Cavity under nave SE	3.3°C		
C. Wall decoration h=3.2 m	26.7°C	20.9%	-2.7 o/oo
D. Wall decoration h=2.4 m			-3.1 o/oo
E. Epitaph h=3.5 m	25.5°C	14.6%	-14.1 o/oo
F. Roof nave NW	25.5°C	22.1%	
G. Floor nave NW	17.6°C	34.9%	
Electric power	21.5kW		



The table shows the situation in Kaupanger stave church on 4 February 1987 at 9.31 am. Heating of the church has led to low RH in the upper parts of the nave. This has resulted in wooden objects in the church drying out and shrinking. The epitaph, which hangs on the north side of the nave, has shrunk 14.1 o/oo since 5 December 1986 when recordings began. The dimension gauge behind the epitaph is 155 mm long. 14.1 o/oo equals 2.2 mm more than the length of the instrument. The drawing to the left illustrates the consequences of such dehydration.

Appendix

Technical specifications of equipment used:

Local computer

Hardware:

Make: Ing. Paul Jørgensen, Trondheim, Norway
Type: EA-2.

- 30 analog inputs 0-20mA
- 10 digital inputs
- 7 digital outputs 300mA/50V DC
- Modem with automatic phone-in and answer
- Charger/accumulator for 6-8 hours of operation if power supply fails
- Real time clock/calender
- Memory for 48-hour storage of data from 30 inputs with recording intervals of 10 min.
- Surge protection from power supply and telephone line
- Temperature controlled heat source for operation down to -30°C

Programmes for monitoring/error warning/remote control/logging out:

- 30 analog and 10 digital inputs + 7 digital outputs
- Warning of error states via bleep paging system/receiver with printer/signal tone on telephone
- Alarm limits/alarm telephones/calibrations/time delays/etc. can be changed by phone
- Error states/instant values/accumulated values can be obtained from any terminal with a modem connected to the telephone network
- Control systems connected to the installation can be started/stopped by telephone
- Passwords protect the system against intrusion

Sensors for recording air temperature/humidity

Make: Vaisala OY, Helsinki, Finland
Type: HMP 123Y

The humidity sensor is based on the capacitive principle of measurement. The sensor is covered with a thin polymer film which quickly reacts to changes in humidity. The range covered is 0-100% RH and the output signal is 4-20 mA in direct ratio to humidity.

The temperature sensor has a maximum measurement range of -40°C to +80°C. Output signal is 4-20 mA. The output uncertainty at +20°C is +/- 0.3°C.

Separate sensors for recording air temperature

Make: Kamstrup-Metro A/S, Åbyhøj, Denmark
Type: Transmitter: 83-23-113
PT-100-sensor: 83-41-213

Measurement range +/- 50°C +/- 1%, output signal 4-20mA.

Sensors for measuring dimensional change in wood

Make: Ing. Paul Jørgensen, Trondheim, Norway
Type: Lise

Measurement accuracy approx. 1/100 mm.
Breadth x height = 10 x 8 mm. Length adjusted to the relevant measurement point. Output signal 4-20 mA.

Meter for recording electric power/electricity consumption

Make: Neuberger, German Federal Republic
Type: Sensor: VJC 3-phase 220V. Output signal 0-20 mA.
Transformer: ZA5-500/5A

TEMPERATURE AND HUMIDITY IN A LARGE GLASS SHOWCASE FOR A TEMPLE HALL

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SUMMARY

Temperature and humidity in a large glass showcase were measured and discussed. The glass showcase contains a historical construction designated as a national treasure, Konjikidō (Golden Hall) of Chūsonji Temple. The climate was measured under the supervision of the Research Committee of Conservation Facilities to improve the air-conditioning system of the glass showcase. Data were obtained at 12 points every hour and stored in a data logger. The analyzed data revealed the invasion of humidity from the ground. The analysis also explained why dewdrops are observed on the glass showcase in early summer. Considering the result, the committee suggested to Chūsonji Temple an improved air-conditioning (RH control) system.

Introduction

Chūsonji Temple located at Hiraizumi, Iwate prefecture was founded in 1105 by Fujiwara Kiyohira, governor of the Northern Province. He intended Hiraizumi as a northern capital, another Kyoto, so much so that Hiraizumi (or Chūsonji) culture has often been called the "mirror of Kyoto culture". Although the twelfth century was a period of wars when the samurai (military) class was taking the place of the aristocracy, Hiraizumi culture flourished under Fujiwara because Hiraizumi is far from Kyoto.

The Konjikidō (a small wooden building) was built between 1109 and 1124 by Kiyohira as a mausoleum for himself and as an Amida Hall (Photo 1). Konjikidō, gorgeously covered in gold leaf, was also a symbol of the prosperity of Hiraizumi culture. In the twelfth century, Chūsonji Temple had about 340 buildings in its compound and several hundreds of people - monks and lords - led their lives there. But many buildings were burned down or laid waste by war in the fourteenth century. Fortunately, Konjikidō remained over the centuries. The remains of Kiyohira, his son and grandson are still mummified now beneath the three altars of Konjikidō.

Konjikidō is a single storey, 5.5m long, 5.5m wide and 8.0m high building. In order to protect Konjikidō, a wooden shelter was built in 1288. During 1962-1968 the present fireproof shelter was constructed with reinforced concrete (Photo 2) and restoration was also carried out entirely on the exterior and the interior of Konjikidō. Due to this restoration, Konjikidō regained its glitter of gold leaves as we see it now.

Konjikidō is settled in a room of the shelter separated from visitors' area by three large glass walls, thus called "a (large) glass showcase" (Photo 3). The dimension is 10.5m long, 10.5m wide and 10m high. The air-conditioning system was equipped to maintain a stable climate in the glass showcase (25 °C,50%RH in summer and 15 °C,40%RH in winter). Since a rapid flow of supplied air caused damages (crack, warp) of members of Konjikidō, the air-conditioning system was stopped in a few years. In 1986, the Research Committee of Conservation Facilities of Konjikidō, chairman Dr.Masaru Sekino, was organized to improve the conservation facilities including the air-conditioning system.

The research committee charged the author to investigate the actual climatic condition within the glass showcase. The subjects were as follows:
1) distribution of temperature and humidity in the glass showcase
2) airtightness of the glass showcase
3) necessity of the air-conditioning system of the glass showcase
4) suitable air-conditioning system, if the system is indispensable
5) cause of dewdrops observed on the glass showcase

Photo 1 Konjikidō (inner view)

Photo 2 Shelter of Konjikidō

Photo 3 Glass showcase of Konjikidō

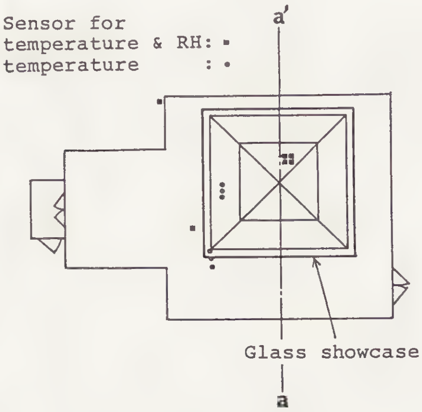


Fig.1 Konjikidō, a glass showcase, a shelter and sensors (plan)

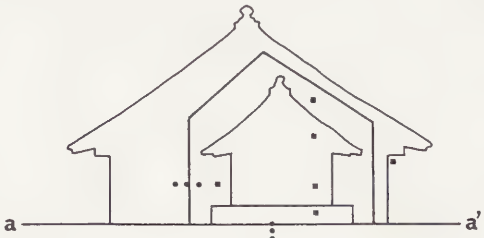


Fig.2 Konjikidō, a glass showcase, a shelter and sensors (sectional plan)

Measurement

Temperature was measured every hour by Pt resistance thermometers at 12 points, while humidity was also measured at the same time by electric resistance hygrometers at 6 points (Fig.1 and 2). Temperature and humidity data were stored in a data-logger (Field Memory, Hayasaka Co.Ltd.) and collected every month by a hand-held computer (HC20, Epson Co.Ltd.).

The collected data were transferred again to a 16 bits computer (PC9801, NEC Co.Ltd.) at the Tokyo National Research Institute of Cultural Properties. Then mean values of each day and month were calculated. The absolute humidity and the dew-point were also calculated to examine the cause of dew.

Result

Figure 3 shows the changes of temperature and humidity in Konjikidō. Oblique lines indicate absolute humidity in mmHg. Numbers by marks are the months when data were measured. The humidity inside descends in September, because dehumidifiers began to work in the glass showcase.
Figure 4 shows the seasonal change of a vertical temperature distribution.
The surface temperature of the glass showcase is plotted against a dew-point in early summer - a rainy season - when dewdrops are often seen (Fig.5).

Discussion

The inside of Konjikidō is always humid (75-80%RH) even in a dry season (March-May) unless air-conditioning is provided. In summer, temperature is 25°C and humidity increases more than 80%RH. The climate suits the growth of mold extremely well and growth was actually observed on a urushi (Japanese lacquer) layer of the walls of Konjikidō from July to August. Thus, an air-conditioning system, a dehumidifier in particular, is necessary for the conservation of Konjikidō.

Figure 3 shows that the absolute humidity of Konjikidō is always greater than that of others. This difference is considerably noticeable in spring. This fact implies the existence of a moisture source in the glass showcase. Since the moisture barrier under the floor is incomplete, humidity rises from the ground. This phenomenon is observed mainly in spring - a dry season - and is indistinct in the rainy season because the invasion of moisture through gaps of the glass showcase is superior to the rising moisture from the ground when the air outside has a high RH.

Changes of temperature in Konjikidō and under the floor cross each other twice in spring and in autumn (Fig.4). Because the bedrock under the floor of Konjikidō has an enormously large heat capacity, the temperature change inside is delayed when compared to the seasonal temperature change outside. This delay causes dewdrops on the glass showcase in early summer. As seen on Figure 4, temperature in the glass showcase is lower than that outside in June and July. The glass cooled by the air inside easily produces dewdrops on the glass surface facing outside, if wind brings humid air whose dew-point is lower than the temperature of the surface (Fig.5). In winter, however, the glass is warmed by the air inside and the humidity in the glass showcase is not quite extremely high enough to produce dewdrops on the glass surface facing inside. Thus, it is clearly explained why dewdrops are observed on the glass surface facing outside only in early summer.

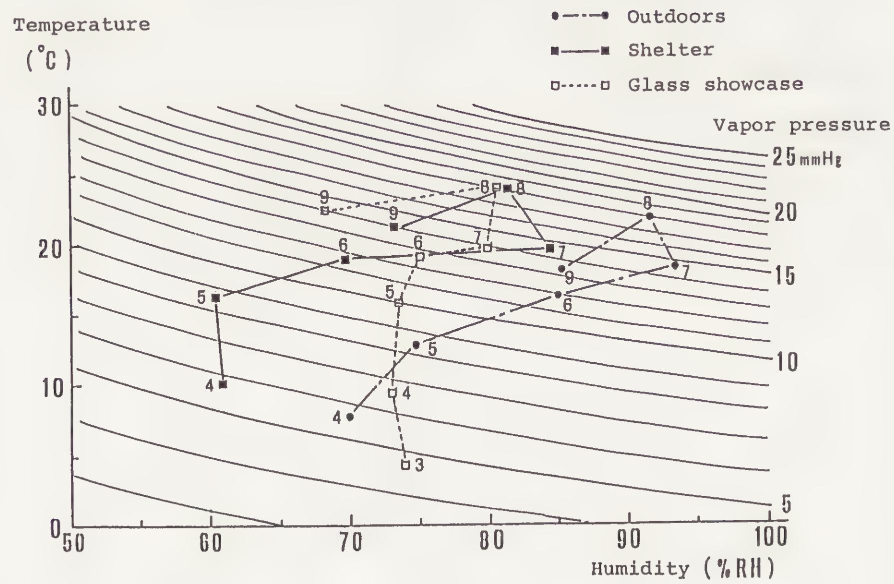


Fig.3 Climate of Konjikidō (March - September, 1986)

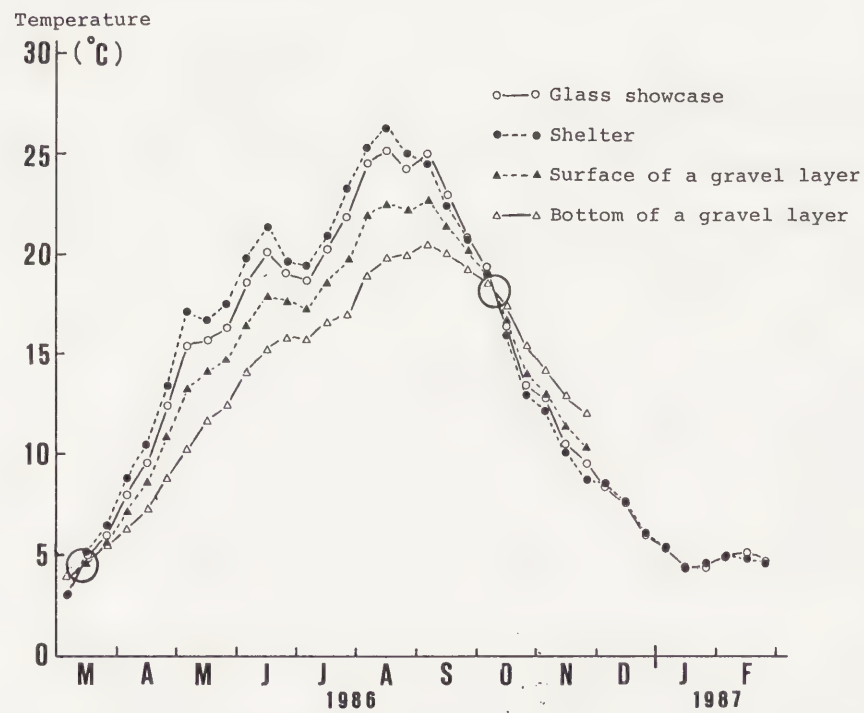


Fig.4 Seasonal changes of temperature in a glass showcase (March, 1986 - February, 1987)

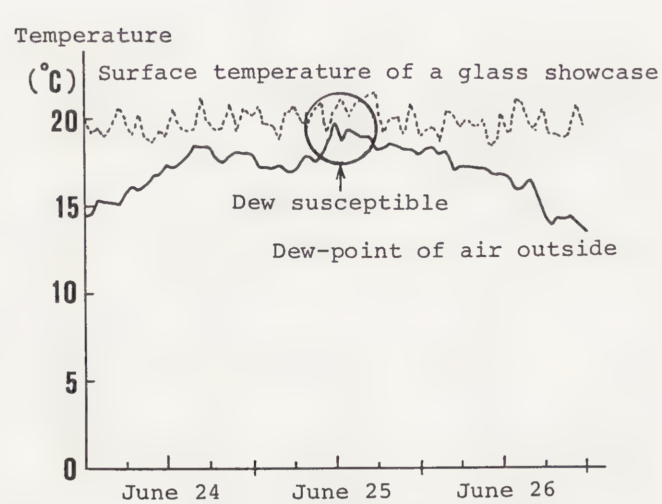


Fig.5 Dew-point and surface temperature of a glass showcase

Proposal For Improvement

Considering this research, the committee made a proposal on a plan of amelioration for the conservation facilities of Konjikidō. The suggestions concerned with the air-conditioning system are as follows:

1) The glass showcase should be improved to make it tighter and to keep RH inside more stable (60-65%RH). All gaps of the glass showcase should be sealed. A moisture barrier sheet is to be laid under the gravels of the floor to isolate the moisture from the ground.
2) Since Chūsonji Temple is located on a hill with plenty of trees and high RH is maintained through the seasons, a dehumidifier controlled automatically by a humidity sensor will be useful to Konjikidō. A humidifier may not be necessary. But a moisture buffering material should be provided to keep RH in the glass showcase more stable.
3) Even when the above improvements are made, dewdrops on the surface of the glass showcase may not disappear if a large difference of temperature still remains between inside and outside the glass showcase. Air-conditioning of the shelter will prevent such a risk. Therefore, air-conditioning systems both for the glass showcase and for the shelter are indispensable to the conservation of Konjikidō. The air-conditioning of the shelter will also be good for the health of the keepers.

Considering these suggestions, Chūsonji Temple and architects planned an improved conservation facilities for Konjikidō. Works began from December, 1986 with financial aid from the Agency for Cultural Affairs.

Acknowledgement

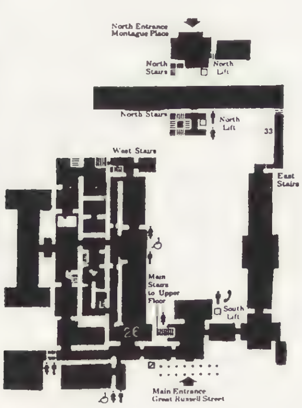
The author would like to express his sincere thanks to the administration of Chūsonji Temple, the members of the Research Committee of Conservation Facilities, especially to Dr.Sekino and Prof.Miyano, staffs of Architecture Division of the Agency for Cultural Affairs and the colleagues at the Tokyo National Research Institute of Cultural Properties, Mr.Emoto and Mr.Ishikawa. He is also grateful to Mrs.Matsubara and Mr.Murakami for their kind helps in accomplishing this paper.

UMMARY

his paper outlines the history of the installation of he dehumidified showcases or the display of corroded opper alloy objects in the epartment of Western Asiaic Antiquities in the ritish Museum.

t discusses in detail two howcases from different xhibition galleries, desribing the method of consruction and the equipment sed to maintain a steady elative humidity value of 0% or less. The associated roblems of monitoring the nvironment and obtaining ccurate readings of relatve humidity and temperature re also considered in an ttempt to assess the uccess of a system which as been in operation for onger than fifteen years.

Upper Floor



Ground Floor

Basement

Fig. 1: Gallery Plans of the British Museum.

17 YEARS OF DEHUMIDIFIED SHOWCASES IN THE BRITISH MUSEUM

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Introduction

In Garry Thomson's book "The Museum Environment" (1) published in 1978, the section on relative humidity (R.H.) illustrates a showcase exhibiting corroded copper alloy objects in the Assyrian Basement in the British Museum as an example of a dehumidified display case. Since then interest has been expressed at ICCROM as to the degree of success in maintaining a low relative humidity in this and similarly conditioned cases in the British Museum. This paper describes the collections which have been displayed and stored in dehumidified conditions, outlines the facilities and the sequence of installation, and presents an interpretation of the relative humidity readings in the cases and storage room.

Historical Background

The Department of Western Asiatic Antiquities holds an extensive collection of corroded copper alloy objects from the Middle and Near East. Many of these were presented to the British Museum by archaeological excavators in the nineteenth and twentieth centuries from such famous sites as Ur and Nimrud. Conservators and scientists have noted over the years that the corroded copper alloy objects from these regions are unstable due to the presence of cuprous chloride. They were already largely or totally mineralised when excavated and now, exposed to the atmosphere, they continue to deteriorate, eventually turning to powder. The reason for their condition is clearly linked to the extremely salty soil conditions in which they were buried; similar deterioration occurs in associated contemporary ceramics. Attempts to stablize the objects using sodium sesquicarbonate (2) or benzotriazole (3) are not successful.

It has long been known that by lowering the relative humidity in the display or storage area to below 45% the process of deterioration of these copper alloy objects can be slowed down or completely arrested (4). As a result, a decision was made in the Department of Western Asiatic Antiquities to maintain a steady environment of less than 40% relative humidity for these objects. A possible conflict of interest between curator and conservator over the display of other materials in showcases containing these sensitive objects, did not arise because archaeologically associated materials such as ceramics, and desiccated organic remains are usually so full of soluble salts that they also require a low R.H.

The first dehumidified showcases were installed at the end of the 1960's on the upper floor of the Museum. They were to house part of a display in the Babylonian Room (No. 54 on plan). The material in these cases included finds from the Royal Tombs at Ur and a neighbouring site, Al U'Baid. In 1971, two conditioned cases were constructed as part of the permanent exhibition in the Assyrian Basement (No. 88/89 on plan) including that illustrated in "The Museum Environment" (Fig. 36). Subsequently, further conditioned cases were built to house the totally corroded remains of the copper alloy Gates from Balawat (No. 26 on plan).

In the mid 1970's additional dehumidified cases were installed in the new Anatolian and Iranian Rooms (Nos. 52 and 51) on the upper floor of the Museum. The latest gallery to be redesigned incorporating dehumidified showcases was the Syrian Room (No. 57) which contains objects from the Later Bronze Age and Iron Age.

Finally, a dehumidified storage room was constructed to house the remaining copper alloy objects from the collections, not on display in the galleries. Details of the installations and the events leading up to them are no longer available. Many of the decisions concerning choice of exhibits, showcases and their dehumidification took place at meetings and it seems that the discussions are not recorded. The following information has been obtained principally by examination of the showcases in the galleries and by interviewing members of the Museums's staff, though however many of the instigators of the systems have now retired.

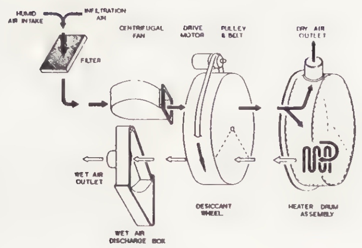

Fig 2: Air flow diagram for dehumidifier (Rotaire M125).

The Dehumidification System

Over the years the equipment chosen has varied slightly due to availability, but the principles of operation remain the same. Humid air is drawn into the dehumidifier by a fan and is dried on the way into the showcase. Re-circulation air is pushed down into the case by a slight pressure difference being set up. Drying of the incoming air takes place in a rotating wheel or drum which contains desiccant crystals. At the same time moisture is removed from the other side of the drying drum by a separate stream of heated air which passes out into the gallery where it is mixed with the outside air.

The operation of the dehumidifier is controlled by means of a humidistat located inside the case, away from the incoming air vent. The humidistat consists of a moisture sensitive material, such as hair or cotton threads, which expand or contract as the R.H. in the atmosphere rises and falls. This in turn is connected to a small make-or-break electrical circuit which switches the dehumidifier on once the R.H. rises above the required level.

Equipment used in the conditioning of showcases in the British Museum

All the dehumidifiers used in controlling the relative humidity in the cases under discussion are manufactured by Rotaire Ltd. Two brands of humidistats have been installed, made by Honeywell and by Sauter.

Gallery/Room	Position on plan	Dehumidifier/ Model No.	Humidistat
Babylonian Room	(54)	M60 (no longer in production)	Honeywell
Assyrian Room	(88/89)	M75 (no longer in production)	Honeywell
Balawat Gates	(26)	M75 (no longer in production)	Honeywell
Anatolian Room	(52)	M125	Sauter
Iranian Room	(51)	M125	Sauter
Syrian Room	(57)	M125	Sauter
Bronze Storage Room	(52)	M125	Sauter

Servicing of the dehumidifiers occurs every six months and is done by an engineer from Rotaire Ltd. The machines contain filters which prevent dust and dirt entering and clogging up the components. These have to be removed and washed in water when they are dirty. This is especially important in areas when the dehumidifiers are not enclosed inside the bases of the display cases. Filter cleaning usually takes place every six months, but can be necessary as often as once a month, depending on the location of the machine. The humidistat is the most vital piece of equipment in the system and requires regular recalibration and cleaning to remove dust and dirt from the hairs or cotton threads. The small electrical contact also needs regular cleaning and occasional replacement.

Calibrating the system

Over the years a procedure has been devised for setting up such a dehumidifier system. Initially, the temperature and relative humidity in the gallery are monitored over twelve months to establish the seasonal variations. The humidistat, which has been calibrated at the required level of relative humidity is positioned in the case and the system started. The relative humidity within the showcase is left to stabilize before the objects are put into it.

Monitoring the conditions in the showcases and storeroom

Routine monitoring of relative humidity and temperature in the showcases is carried out on a daily basis. Each conditioned case contains a hair hygrometer which is read, normally at the same time each day, and the results plotted. In 1985, a small hole was drilled in the baseboard of each case so that a humidity probe could be inserted inside occasionally to check on the conditions without disturbing the environment. When not in use, the hole is sealed with a plug. To obtain a continuous record of conditions

over a short period of months or weeks, recording thermohygrographs have occasionally been put into the cases.

Written records exist of the relative humidity and temperature in the conditioned cases from 1974 and so it is possible to draw some conclusions about the effectiveness of the dehumidification system chosen and say where or how problems have arisen.

It is probably easier to assess the effectiveness of the system by looking at two examples from different galleries in the Museum. One is the original case from the Assyrian Room illustrated in "The Museum Environment". The other is from the Anatolian Room on the upper floor of the Museum.

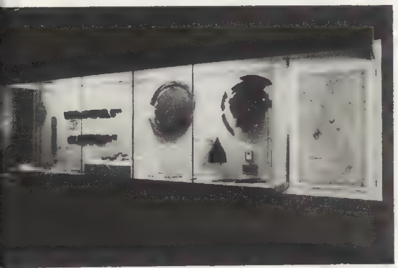

Fig 3: Arms and Armour Case.

"Arms and Armour" Case: Assyrian Basement

This case, containing examples of early technology and weapons mostly of bronze, was purpose built to house a particular display. It is made of steel framework holding glass windows and there are two hinged doors in the front of the case. The glass is stuck into the frames with a putty-like substance and there is a velvet sealing strip down the edges of the doors, which slightly overlap the adjacent glass panels when closed. The lighting box is above the display and separated from it by a layer of plastic diffuser. The dimensions of the case interior are 2.34 m x 1.38 m x 0.5 m and the volume of airspace is 1.9 m^3. The whole case is mounted directly onto a free-standing hollow back wall which divides off part of the main gallery. The dehumidifier, a Rotaire M75 is sited inside the brick structure and is connected to the vents in the back wall of the display case by flexible metal ducting. The machine has a maximum flow rate of 127 m^3/h and its power rating is 600 watts. This particular system has been in operation for longer than fifteen years maintaining a relative humidity that does not vary by more than 6% in a twelve month period and does not usually rise above 40%.

Fig 4: Case 6 Urartu.

Case 6: Urartu, Anatolian Room

The Anatolian Room is on the upper floor of the Museum and is one half of a large gallery on the east side of the building. It is a room with a high glass roof which is concealed above a suspended ceiling. The showcase is one of a standard design issued by the Department of the Environment for use in museums and galleries. It contains copper alloy and lead objects from Toprakale in Urartu. The showcase consists of an extended aluminium framework holding glass panels which are secured with a plastic sealant. There is one hinged door which forms the end of the case. As with the previous showcase, the lighting is in a space above a layer of plastic diffuser. The dimensions of the exhibition space for this showcase are 1.75 m x 1.175 m x 0.85 m and the volume of airspace is 1.7 m^3. The case is mounted on a wooden plinth which conceals the Rotaire M125 dehumidifier. Dry air is pumped into the case via

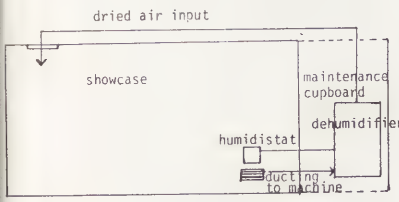

Fig 5: Diagram of dehumidification system for Arms Case.

Fig 6: Dehumidifier in maintenance cupboard next to Arms Case.

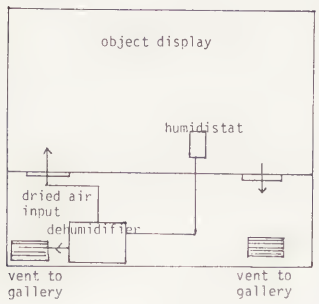

Fig 7: Diagram of dehumidification system for Case 6.

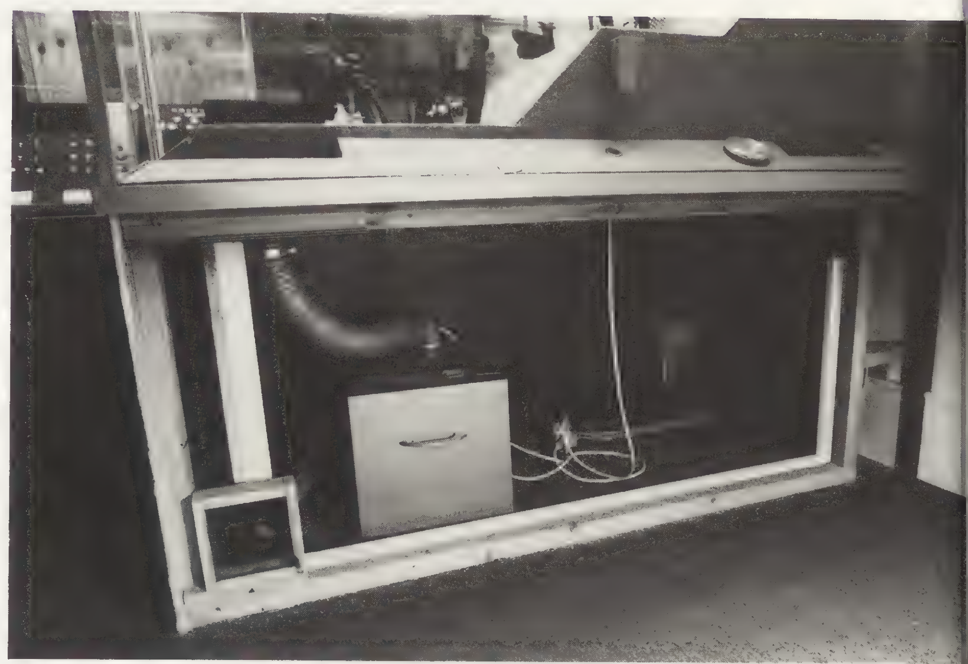

Fig 8: Dehumidifier in the base of Case 6.

flexible metal ducting connected to aluminium vents in the baseboard of the display. The design of the system was done by Rotaire Ltd and the conservator from the Department of Western Asiatic Antiquities. Installation took place in 1976 after the completion of the exhibition by the Design Office of the British Museum. Sufficient space had been allowed for the required vents and trunking to be incorporated in the layout of the interior of the showcase.

The Rotaire M125 has a maximum flow rate of 125 m^3/h and a power rating of 750 watts. Readings taken over the years indicate that the relative humidity varies by as much as 10%, occasionally reaching as high as 45% and the plotting of the values indicates that the machine is switching on and off more frequently than that in the Assyrian Basement.

Factors which affect the System

1. Showcase Construction

It is important that any conditioned showcase is well sealed to reduce the exchange of dehumidified air with that in the gallery outside. One that has been constructed for this specific purpose is likely to be more effective than one which was adapted. Many well constructed showcases maintain a non-fluctuating environment inside them without the need for conditioning at all. A poorly sealed showcase will also allow dust and dirt to enter which can affect delicate mechanisms and of course, the collections.

2. Humidity Registering Devices

The dehumidifier is controlled by a humidistat which contains hairs or cotton threads. Both of these materials eventually lose their sensitivity and their calibration changes, and this can be accelerated if dust or dirt settles on them, so they require regular checking and cleaning. Similarly, the small electrical contact may need cleaning or replacement, particularly if the dehumidifier is switched on and off frequently. Similarly, the hair hygrometers monitoring the system lose their calibration and need attention.

A random check made on the conditioned cases one morning in January 1987 by taking a relative humidity reading from the hair hygrometer inside the case together with one using the humidity probe. At the same time the dial setting on the humidistat was noted. The readings were as follows:

	Hygrometer	Humidity Probe	Humidistat
Arms Case	44%	34%	25%
Urartu Case	34%	32%	42%

If the humidity probe, which works by measuring the resistivity of an R.H. sensitive element, is taken as the most accurate measuring device it can be seen that the hygrometers can vary by as much as 10% from the true relative humidity (if not regularly calibrated). However, even if out of calibration, they can still provide a guide to the general condition in the case as they continue to indicate excessive variations in the conditions in the case. Likewise, the humidistat will continue to control the dehumidifier and maintain the relative humidity at the required level if it is regularly calibrated. The readings quoted earlier are those from the 1970's using the hair hygrometers. They do provide a guide to the ability of the system to maintain a steady environment.

3. The Dehumidifier

Provided that the machinery is regularly serviced and the filters checked and cleaned, it would appear that these are entirely satisfactory.

4. Environmental Conditions in the Gallery

Early in 1987, recording thermohygrographs, that measure R.H. using stretched hairs, were placed inside each of the two cases and outside in the respective galleries. Charts from the week 26 February to 4 March are illustrated below, unbroken lines indicate readings from the gallery, broken line readings from inside the showcases. The following points may be seen from the results.

The Assyrian Basement is surrounded by other galleries and rooms in the middle of the Museum. The temperature can be seen to be steady at around 20°C with few fluctuations. (Fig 9) The R.H., (Fig. 10) however, does vary between 55% and 28% but not on a daily cycle. The R.H. in the gallery is related to the R.H. outside the Museum and will change with that. Inside the dehumidified case the R.H. remains steady at around 25% rising gradually to 27%, but the temperature follows a diurnal cycle probably responding to the heat evolved by the case lights, which are switched on in the morning and off at night. It is interesting to note that the R.H. corresponds to that set on the humidistat.

The Anatolian Room is on the upper floor of the Museum, one of its walls being the outside wall of the building. It is one of the main routes between the front and back of the Museum. The temperature readings both inside and outside the case follow the same pattern, reflecting the Museum's heating cycle, with the additional effect of the lighting inside the case.(Fig 11)

The R.H. of the gallery varies between 52% and 38% and that inside the showcase between 37% and 41%.(Fig 12)

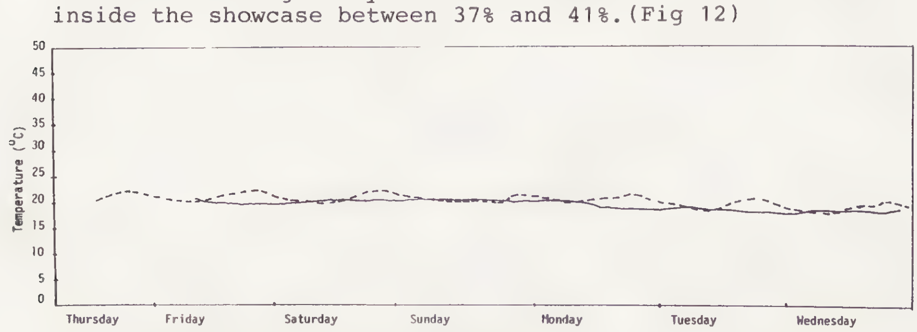

Fig 9: Temperature Readings from the Assyrian Basement, 26 February - 4 March 1987

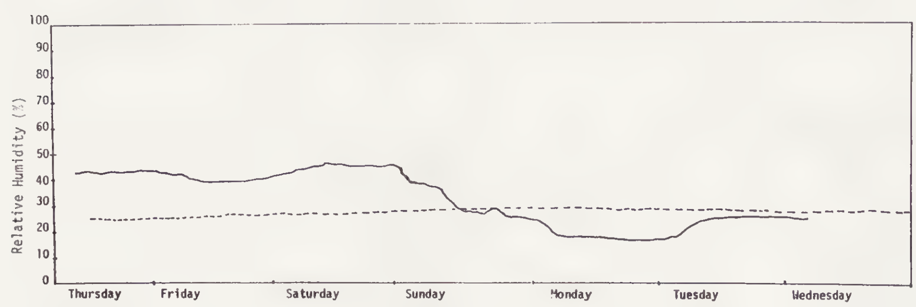

Fig 10: Relative Humidity Readings from the Assyrian Basement, 26 February - 4 March 1987

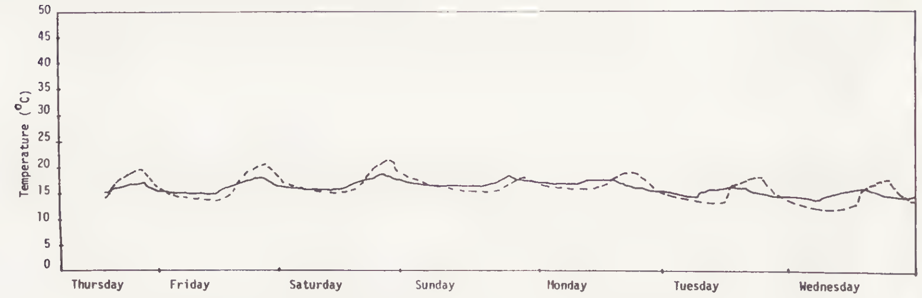

Fig 11: Temperature Readings from the Anatolian Room, 26 February - 4 March 1987

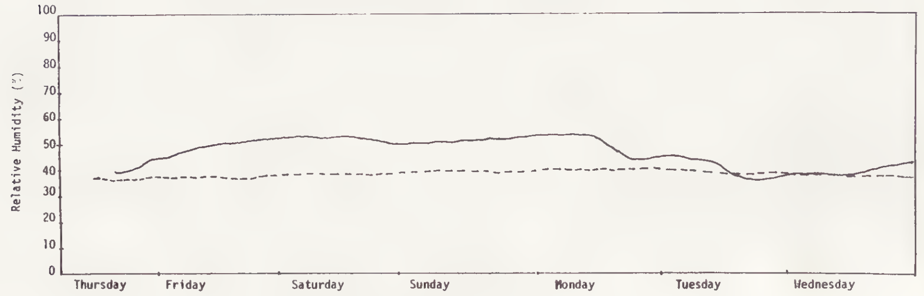

Fig 12: Relative Humidity Readings from the Anatolian Room, 26 February - 4 March 1987

In the original charts taken from the recording thermohygrographs it is possible to see small inverted peaks that indicate the dehumidifier is switching itself on and off - responding to the humidistat. This appears to happen three times a week in the charts from the Anatolian Room case, but is undetectable in the Assyrian Basement case. It should be noted that readings illustrated above were taken during what was an exceptionally dry period in London.

Conclusion

It is clear that the ideal showcase to condition is one which is both well sealed and stands in an already stable environment. As the gallery becomes more unstable the equipment has to work harder to maintain the required conditions.

The most vital piece of equipment in the system is the humidistat. It monitors the environment and then switches the dehumidifier on or off. The type of humidistat in use at the present time has a number of limitations which lead to loss of accuracy. The use of organic moisture-sensitive material means that regular cleaning of the hairs or thread is essential. The calibration must also be checked regularly against an accurate R.H. measuring device. Cleaning of the small electrical contact and its eventual replacement when it wears out may be necessary.

It is possible that if another type of humidistat was available the relative humidity level within the showcase might remain steady with fewer variations. Over the years the dehumidified showcases in the British Museum have proved successful in helping to prevent the deterioration of potentially active copper alloy objects in the Department of Western Asiatic Antiquities. The system is not perfect and as technology improves, it may be possible to produce the ultimate in stable, conditioned showcases.

Acknowledgements

The success of the dehumidification system is due mainly to the perseverance and experience of the conservators originally in the Department of Western Asiatic Antiquities, in particular, Mr J Bateman, who provided so much of the information on which this paper is based and Mr C Bateman. I would like to thank Dr V Daniels and Mr W Oddy of the Department of Conservation for their general assistance and encouragement to publish and also the Department of Western Asiatic Antiquities for their help in providing background information on the history of the galleries.

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THE SPONTANEOUS TRANSFER TO GLASS OF AN IMAGE OF JOAN OF ARC

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SUMMARY

A woven silk picture transferred its image to the glass against which it had been pressed for fourteen years. The image was formed from salt, which occupied the areas where the silk had not touched the glass. Salt impregnation increases the water absorption of silk at a relative humidity below the value at which pure salt deliquesces. A salt solution had formed in the fabric at a moderate relative humidity and then migrated to the glass where the salt precipitated because the relative humidity was below the deliquescence point of pure salt. The process has been replicated.

It is not unusual to find on opening the glazed frame of a picture that an image of the original has been imprinted on the inner surface of the glass. Here we propose an explanation for one example of this phenomenon.

The silk picture shown in Figure 1 was woven by the Jacquard process in France around the beginning of this century. It now belongs to the National Museum of American History in Washington DC [1]. This picture and six others from the same source were framed pressed against glass. They hung for seven years in a curator's office, after which they were put into a store room for a further seven years. When the frames were dismantled each glass was seen to have acquired a copy of the original picture.

The image, shown in Figure 2, results from the scattering of light by fine crystals of salt, sodium chloride, which form an adherent film on the inner surface of the glass. The salt is mixed with a small amount of an organic substance with surfactant properties. The dark areas are clear glass. The white areas of salt on the glass match the white areas on the picture almost exactly. There is, however, a notable exception: the sleeve of the left arm (Figure 3, top). Here a dark mark on the glass (Figure 3, middle) corresponds to a glossy white area on the woven image. Figure 3, bottom, is a relief image of the cloth which shows that all the dark areas of the picture, but only a few of the white areas, including the highlight on the sleeve, are raised. The salt image does not match the pattern of the colour but instead follows the relief of the original. The salt is found on the glass only where the cloth did not touch it.

Figure 1: The woven silk picture of Joan of Arc. It measures 520 by 320 mm.

Figure 2: The image on the glass which was pressed against the picture. The pale areas are formed by light scattered from fine salt crystals.

Figure 3 (left): An enlarged portion of Figure 1 (top) with the salt image (middle) and the surface relief of the silk (bottom).

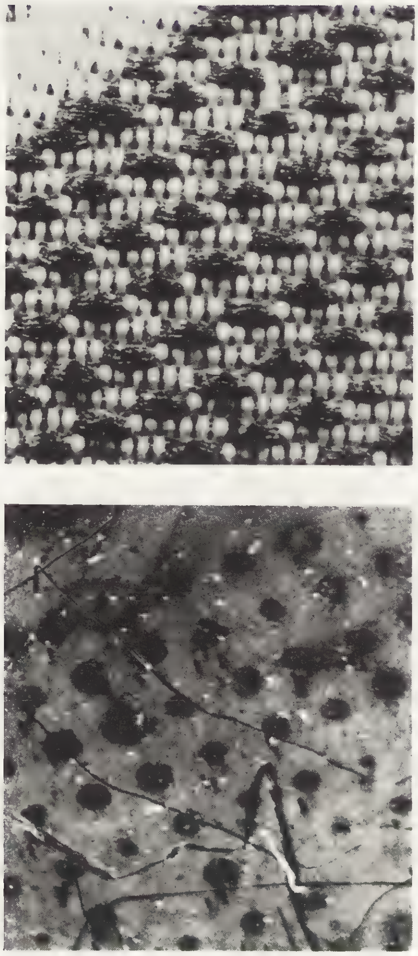


Figure 4: The crystallization pattern of an evaporating salt solution with surfactant.

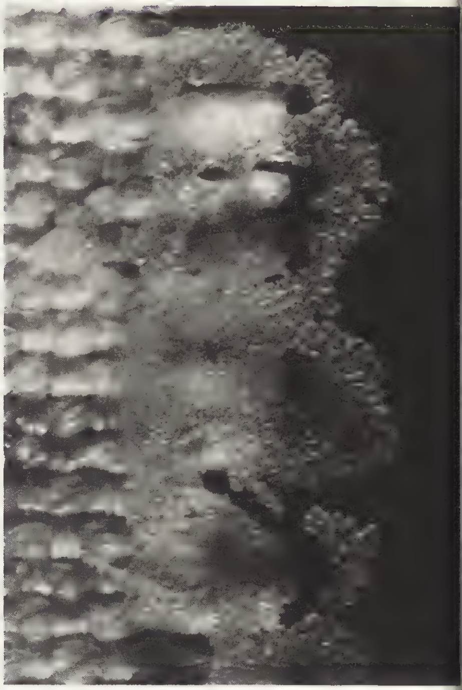


Figure 5: The pattern of salt formation on glass resulting from migration and evaporation of solution from saturated silk.

Figure 6: A portion, 10 mm across, of a companion picture to Joan of Arc (top), and the corresponding salt image.

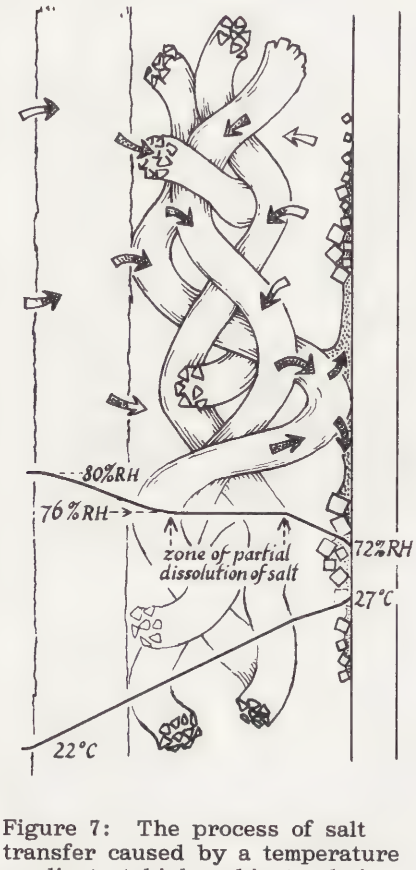


Figure 7: The process of salt transfer caused by a temperature gradient at high ambient relative humidity.

The image on the glass is consistent with crystallization from a salt solution containing a trace of surfactant [2]. Figure 4 shows how crystals form over the glass of a beaker containing such a solution. Note how there is a gap between the surface of the solution and the lowest crystals on the glass. This gap is shown more clearly in Figure 5. Here a piece of silk, saturated with salt solution, is placed against a piece of glass. As evaporation proceeds crystals form on the glass at a small distance from the point of contact of glass with silk. Figure 6 shows a portion of a companion picture to Joan of Arc and the corresponding salt image. The clear area on the glass around the point of contact with the silk is clearly shown.

Salt is widespread in the picture assembly. It is in the silk cloth, in the linen behind the silk and in the card backboard. The salt could have transferred to the glass during a period of high relative humidity (RH). Above 76% RH pure salt deliquesces: the crystals absorb water vapour from the air and dissolve to form a saturated solution.

A possible sequence of events within the frame of the picture of Joan of Arc is illustrated in Figure 7: as humid air diffuses slowly into the picture from the back, water absorption by the salt crystals buffers the relative humidity so that until all the salt has dissolved the relative humidity of the air within the enclosure cannot exceed 76%. Suppose now that a temperature gradient forms within the picture because its back is against a cool outside wall or because the front is warmed by a spotlight. The relative humidity at the back of the picture will be buffered to about 76% by the action of the salt, whose deliquescence point is not affected by temperature. However, the relative humidity at the warmer inner surface of the glass will be slightly below 76% because in an empty, closed space it is the water vapour concentration which tends to become uniform, not the relative humidity. Under these conditions the salt solution in the fibres will move by capillary flow among the fibres and then migrate from the point of contact across the glass. The salt solution begins to dry out as it traverses the glass, eventually depositing salt at a small distance from the point at which it emerged from the fibres. The evaporated water diffuses back through the picture and the cycle of deliquescence, capillary movement, evaporation and precipitation continues. The first deposit of salt crystals on the glass forms a capillary network allowing the solution to flow outward from the point of contact protected from evaporation. Fresh salt precipitates outside the existing fringe of salt. Over several years even a feeble movement of salt driven by intermittent imposition of a high relative humidity and a small temperature gradient may indeed have generated the image found on the glass.

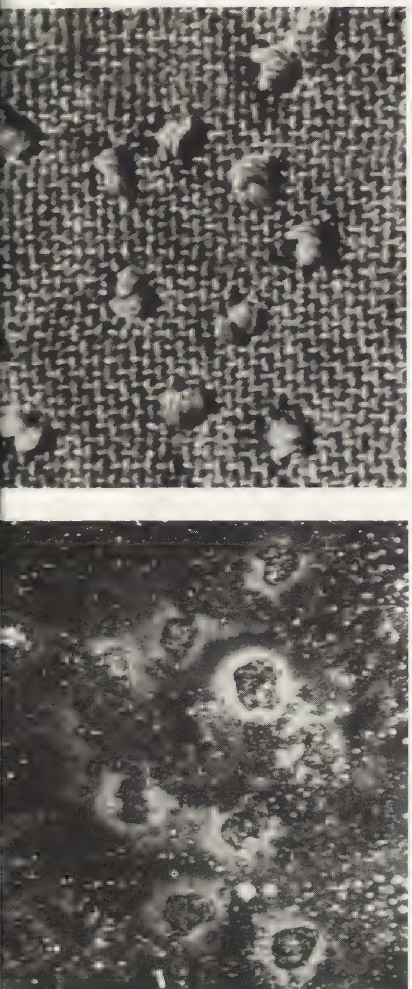


Figure 8: The experimental silk cloth with the image formed on the glass (10 mm across).

Figure 9: The faint salt image on glass formed over two weeks in a constant environment of 65% RH and 22°C. The image is 3 mm across. The bright discs are unfocussed dust particles.

Figure 8 shows the result of a laboratory simulation of the image transfer process proposed in Figure 7. A piece of silk cloth was made uneven with loops of silk thread. This cloth was put in a glazed frame with linen backcloth and card to imitate the construction of the original, except that an impermeable back was added. The silk alone was impregnated with salt. All the components were pre-conditioned to 76% RH by suspending them over saturated sodium chloride solution. After this the pieces were assembled and set on the laboratory bench. The glass was overlaid by a sheet of black paper which was warmed by a lamp. The back of the picture was maintained at the 22°C ambient temperature by fanning air over it. The slight increase in temperature of the silk would, if no salt were present, cause a small increase in the relative humidity of the air in the enclosure. In this case, however, the salt buffered the relative humidity by absorbing the water vapour released by the silk. After fourteen days the piece was disassembled and photographed. Figure 8 (bottom) shows the image on the glass. The similarity to the genuine effect is close, though the process has been arrested at an early stage in the spreading of the fine-grained salt layer out from the clear portion close to each point of contact.

This salt image was formed quite rapidly at about 76% RH, the minimum value at which pure salt deliquesces. However, a relative humidity as high as 76% should never have occurred, at least not for long, in an air conditioned museum. We therefore set up an experiment to see if image transfer could occur at a lower relative humidity and at a uniform temperature.

In this second experiment the test picture was conditioned to 65% RH and then assembled as before. After two weeks of incubation at 22°C salt transfer was again observed. The effect was weaker; indeed the salt was scarcely visible. The image shown in Figure 9 was photographed in a humidity chamber so that the fine salt deposit deliquesced to give liquid droplets which scattered light better.

The silk was examined to determine the distribution of the salt, originally homogeneously distributed within the fabric. We found that it was now concentrated at the high points of the weave, where the cloth touched the glass. It is not obvious why this should be so. However, the authentic images, such as Figure 6, show a small pip of salt at the point of contact, surrounded by the clear halo. Whatever the process at work, there is no inconsistency between the original and the reproduction.

How can salt move, apparently in solution in water, within cloth that is dry to the touch, at a relative humidity well below the deliquescence point? To gain more evidence we measured the water absorption of salt-impregnated silk as a function of relative humidity. The results were surprising. It seems that salt-impregnated silk does not behave like a simple mixture of salt and silk. The diagrams in Figure 10 show what happens. In the case of clean silk there is a continuous absorption of water as the relative humidity increases. The shape of the graph for pure salt is completely different: there is negligible absorption of water as the relative humidity rises until the critical value of 76% RH is reached. At this point the salt absorbs water from the air and dissolves in it to form a saturated solution. As the relative humidity rises further the salt solution continues to absorb water, theoretically reaching infinite dilution at 100% RH. One might expect to describe the behaviour of a mixture of salt and silk by adding together these two curves to produce the composite curve in box C. In fact, however, the step in the curve is smoothed out so that the contaminated silk absorbs more water than expected at a low relative humidity, as shown in box D. Above 76% RH the water absorbing capacity of the mixture is less than expected.

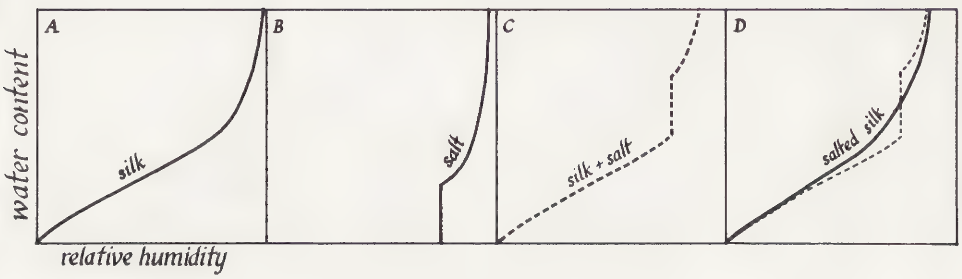


Figure 10: Comparison of the water absorption of silk and of salt: separate and mixed.

Table 1: Water content of silk (percent of dry weight) at 25°C.

RH	clean silk	silk plus 46% salt
9	2.1	2.3
26	4.7	5.1
35	6.0	6.7
45	7.5	8.5
56	9.2	10.9
67	11.4	15.2
70	12.8	20.0
72	13.5	30.7
73	13.9	67.3
67	13.5	21.0
56	11.7	14.1
45	9.9	10.8
35	7.8	8.2
26	6.5	6.6
9	3.3	3.3

RH	clean silk	silk plus 3% salt
15	4.4	4.3
20	5.2	5.1
26	6.0	5.9
32	6.8	6.7
38	7.8	7.6
47	8.5	8.6
54	9.4	9.5
58	9.7	9.9
64	10.4	11.1
71	11.6	13.7
78	13.5	17.8
83	14.5	20.4
93	20.0	33.5
84	17.6	23.0
78	15.8	19.6
75	15.3	18.4
72	14.7	17.3
68	14.1	16.2
65	13.8	15.5
63	13.1	14.3
58	12.5	13.2
53	11.9	12.2
40	9.9	9.8
29	8.4	8.2
20	6.6	6.5

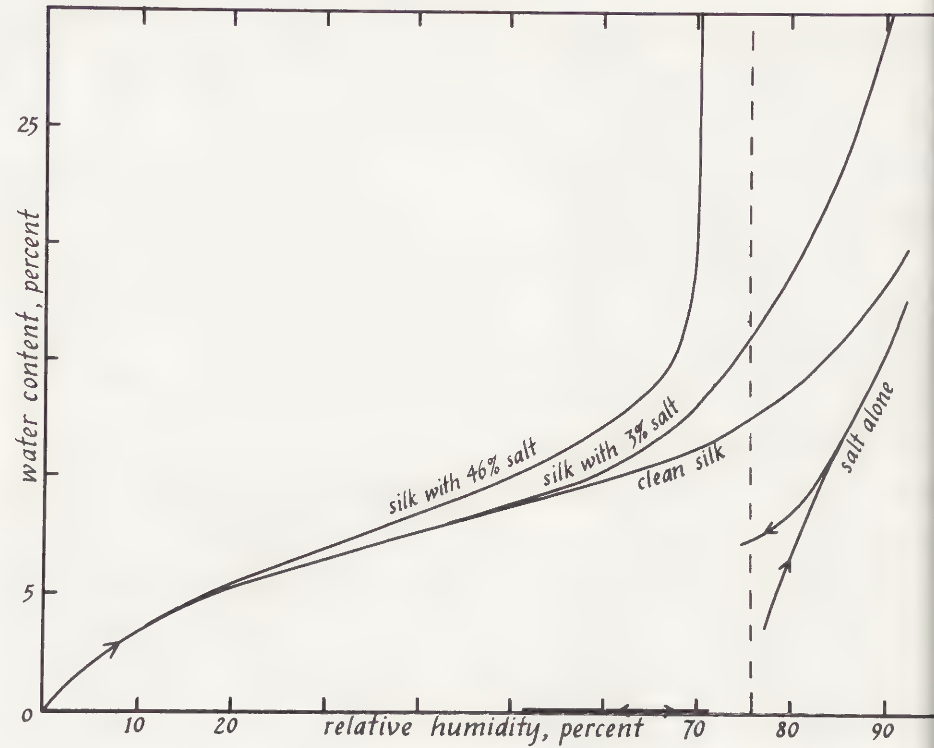


Figure 11: Water absorption isotherms at 25°C of pure silk and of salt weighted silk. The isotherm of pure salt is expressed as grams of water per 3 grams of salt to match the data for 3% salt loaded silk.

Some of our experimental results are shown in Figure 11 (all the measured values are given in Table 1). With very heavy salt contamination the extra water uptake becomes measurable at 25% RH. A three percent loading of salt causes separation of the two curves at about 55% RH.

This extra water is not necessarily mobile. To confirm the existence of an ionic solution we measured the relative humidity dependence of the electrical resistance of silk containing 2.4% salt (Table 2). The results are plotted as conductivity in Figure 12. The electrical conductivity is enhanced in a manner very similar to the water absorption. There is no sudden change of conductivity at 76% RH. Electrical conductivity of the contaminated silk becomes measurable at a relative humidity well below the deliquescence point of salt while that of clean silk remains very small.

It is quite clear from these measurements that salt and silk interact when mixed to form a system with a response to atmospheric moisture unlike that expected from adding the separate contributions of the components.

Table 2: Electrical resistance of silk containing 2.4% of salt.

RH	Mohm	RH	Mohm
37	>7	37	>7
47	>7	60	5.4
53	7	66	3.3
57	6.8	71	2.3
61	5.4	75	1.1
63	4.5	80	0.46
66	3.0	85	0.17
73	1.6	89	0.084
74	1.0	90	0.072
75	0.72	84	0.21
76	0.62	77	0.76
		74	0.74
36	>7	69	1.25
60	6.5	68	1.4
68	3.6	63	2.6
73	1.6	60	4.2
77	0.65	59	4.8
79	0.52		
87	0.12		
80	0.36		
76	0.74		
73	0.64		
72	0.77		

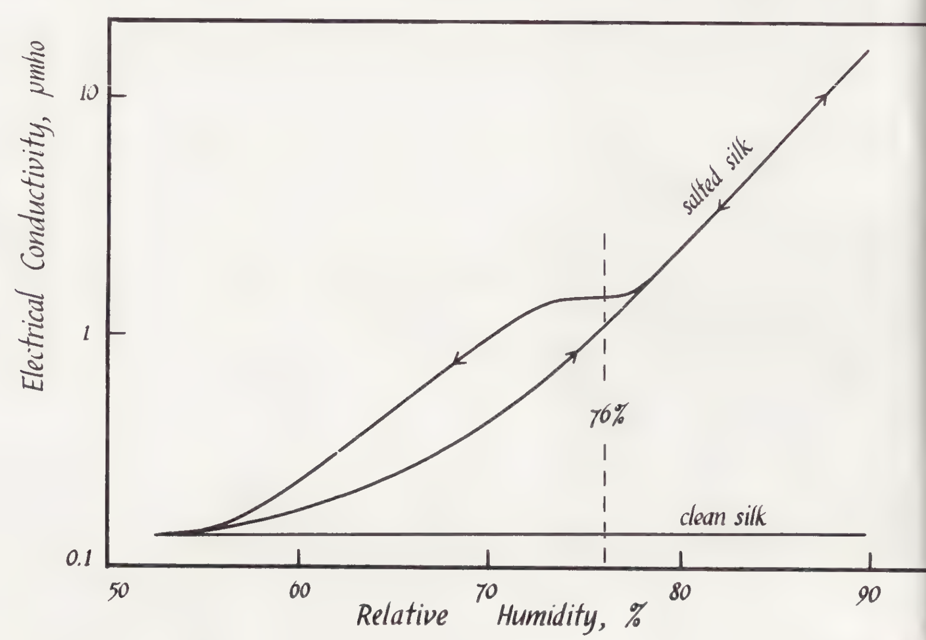
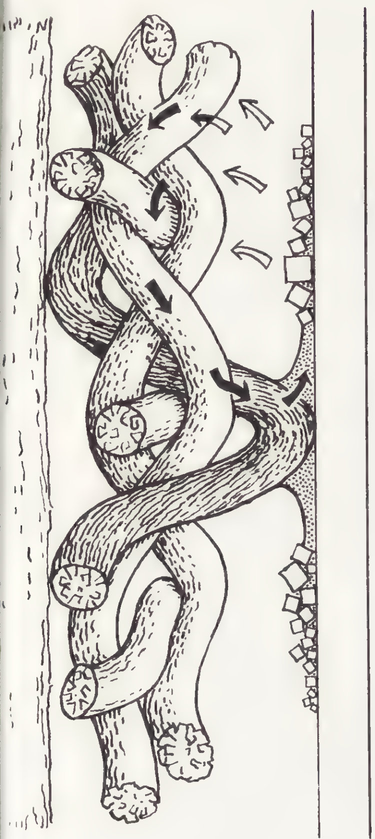


Figure 12: The electrical conductivity of a silk strip impregnated with 2.4% salt, measured at 20°C. The strip was 16 mm wide by 85 mm long and weighed 330 grams per square metre.



gure 13: Diagram of the salt ansfer process at constant and iform temperature.

These results suggest a mechanism for salt transfer that needs no external driving force such as a temperature gradient. This is summarised in Figure 13. The salt-contaminated silk absorbs more water from the atmosphere than pure silk. An electrolyte solution is formed within and among the fibres which is sufficiently mobile that it permeates by capillarity, or by surface diffusion, throughout the entire system. At the point of contact between fibre and glass the solution creeps over the glass. Once free from the fibre the normal deliquescence point of pure salt reasserts itself and the low relative humidity (that is below 76%) causes the solution to evaporate. The salt remains on the glass, the water vapour diffuses to the fibre and the cycle repeats itself. The end result is a transfer of salt from fibre to glass.

The ability of salt to move in solution within a protective capillary network at quite a low relative humidity is demonstrated by the crystals forming in an ambient 50% RH outside the rim of the beaker shown in Figure 4. A salt image, though slow to form at a low relative humidity, is more likely to endure under these mild conditions because the salt separated out on the glass has no tendency to revert to a liquid form unless the local relative humidity exceeds 76%. This second, isothermal mechanism, though slow, is the more plausible explanation for the image of Joan of Arc.

The two mechanisms for salt transfer both require that the glass surface be below 76% RH. They differ in the way a salt solution develops in the fibres. The first mechanism relies on a temperature gradient to produce a relative humidity of 76% in the fibres, a condition which causes even pure salt to deliquesce. The second, isothermal, mechanism depends on the formation of a solution in salted silk below 76% RH. This development of an ionic solution at a low relative humidity is not unique to silk. Cotton contaminated with salt also shows enhanced water absorption. This property may turn out to be a general attribute of hygroscopic solids contaminated with inorganic salts.

The presence of an ionizing liquid has long been known to accelerate reactions on the surface of materials. For example, salt solutions enhance corrosion of metal surfaces [3]. We have found that contamination with a salt solution accelerates corrosion of marble by acetic acid vapour [4]. These reactions occur upon the surfaces of materials that are basically impermeable even though they may be porous on a gross scale. Here the normal deliquescence point of a salt applies. The same acceleration of degradation reactions may occur in hygroscopic organic materials, but at a relative humidity much lower than the deliquescence point of the pure salt. Contaminants which would normally be considered dry and inert at normal museum humidity may really be mobile and reactive, without showing symptoms such as sweating and darkening which occur when salts deliquesce in non-hygroscopic materials.

Deliquescent inorganic salts are widespread in museums. They may be original components of objects, contaminants acquired from use, reaction products of gaseous air pollutants, deliberate additions during treatment or the unconsidered by-product of preservative treatment. Their presence must have an important effect on the permanence of materials.

Acknowledgements

Walter Hopwood, Martha Goodway, Joan Mishara and Harold Westley helped with the analytical work on the silk pictures. We are grateful for help from Rita Adrosko and Kathy Dirks of the National Museum of American History.

NOTES & REFERENCES

1. The silk picture of Joan of Arc was designed by G. Doyen and woven by Neyret Frères of St. Étienne in the early 20th century. There are seven pictures in the set owned by the Department of Social and Cultural History of the National Museum of American History.

2. We used a saturated salt solution with 1% of sodium di-octyl sulfosuccinate for all the experimental work. A full account of the analytical and experimental work together with a more detailed commentary on the results is available as Conservation Analytical Laboratory report no 3349 (1987).

3. U.R. Evans, The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications (London: Edward Arnold Ltd., 1960) pp. 486-501.

4. Work in progress in our lab. Acetic acid vapour in a stream of air at 70% RH reacts much faster with a piece of marble which is contaminated with a small amount of sodium bromide solution than with pure marble. Sodium bromide deliquesces at 54% RH.

UMMARY

he three ways in which emperature and relative umidity are measured in ational Trust houses are escribed. The most recent f these, battery-operated lectronic data loggers, have een an innovation. They ave vastly increased the mount of information on onditions and have enabled mprovements to be made to he environment in many of he 200 houses.

hree case studies llustrating methods of irect control of relative umidity using dehumidifiers re described. The first nvolves a storage area in a ouse undergoing restoration, n which a Polythene 'tent' as constructed and the elative humidity controlled ithin it, using a refrig-rative dehumidifier. The econd describes the control-ing of the environment nside a Perspex display case ontaining a green baize and ilk embroidery textile, by irculating dry air from a eservoir produced by a ehumidifier. The final ase study shows the mportance of draught-roofing for the successful se of dehumidification in a uilding.

inally, the possibilities or controlling relative umidity by temperature are iscussed and found to be articularly suitable for ost rooms in historic ouses.

TEMPERATURE AND RELATIVE HUMIDITY MEASUREMENT AND CONTROL IN NATIONAL TRUST HOUSES

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1. Introduction

The National Trust for Places of Historic Interest and Natural Beauty (usually known as the National Trust) was founded in 1895 as a private charity. It is now the third largest land owner in the country, owning about quarter of a million hectares of land, including 800 kilometres of coastline and some 200 historic houses, in England, Wales and Northern Ireland.

The conservation of historic houses and their contents has only needed to develop within the National Trust since the first country house was acquired in the 1930's. In the early days it was assumed that preservation of the contents of the houses would be achieved by good housekeeping; the need for a more positive attitude only became apparent later. Up until the 1970s the National Trust had no conservators on the staff; conservation advice was often given by the staff of National Museums, and the work carried out by freelance conservators.

By the mid 1970s the need for conservators on the staff had become pressing and an Adviser for the Conservation of Paintings and a Housekeeper were appointed. They were rapidly followed by the setting up of three workshops for the conservation of textiles. There are now sixteen members of staff in the National Trust Conservation Department covering most fields of conservation, still very few for the size of the collections, but enough to have a considerable impact on the care of the contents of the houses.

There are five Housekeepers who, in addition to their responsibilities of training the staff in the houses in the methods of handling and cleaning the furnishings, which are nearly all antiques or works of art, arrange for environmental conditions to be recorded and seek advice on remedial measures if the conditions are found to be unsatisfactory. The 'Bible' of the housestaff is the National Trust Manual of Housekeeping (1), and readers of Chapter 1, 'The Right Environment', will find many familiar words in it, as Garry Thomson helped the National Trust for many years before his retirement.

In practice we have had to widen our specifications a little, as the type of environmental control measures practised in museums can hardly be applied in historic houses; air-conditioning ducting can seldom be accommodated within the architecture. We aim to keep relative humidity (RH) within the range 50-65%. Temperature (T) control is less important, particularly as all the houses are closed to the public from the end of October to the beginning of April. There is only a limited need to heat the houses to temperatures suitable for cleaning and maintenance work during the winter, and for background heating to reduce natural indoor RH to safe levels.

2. Measurement of temperature and relative humidity

Regular recordings of temperature and RH in the houses were started in 1984, as described in the following section, 2.1. Since then monitoring of the environment has progressed with leaps and bounds as the National Trust has started using electronic data loggers.

2.1 Weekly spot readings

Every National Trust house has a residential Administrator, the larger ones also have a residential Custodian. These staff are responsible for keeping weekly records of temperature and relative humidity readings. As their duties in the houses are so many and various it is only reasonable to ask them to take readings on one day each week. These readings are taken in at least four rooms in the house (if possible from rooms facing the four points of the compass) and outside. They are recorded between 0800 and 0900 in

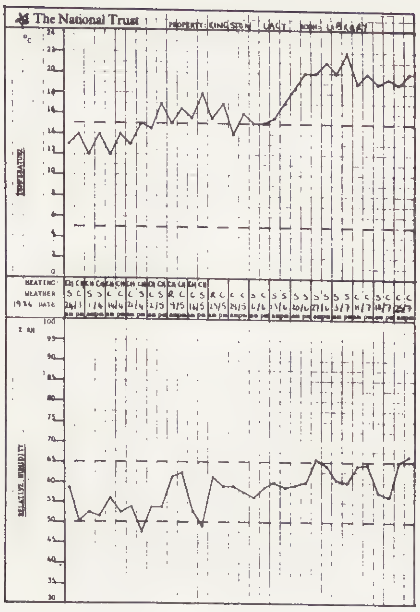

Figure 1

Temperature and relative humidity spot readings from Library in Kingston Lacy, March - July 1986

the morning, and between 1500 and 1600 in the afternoon, and a plotted on a graph, a typical example of which is shown in Fig In addition the staff are asked to indicate the weather conditio and whether the heating is on or off. When a graph is completed is sent to the Conservation Department for advice on action th should be taken if the relative humidity is unsatisfactory. The readings are either taken using a whirling hygrometer (2) or electronic instrument (3).

There are several problems with having such limited informati about conditions within the houses, the most obvious being wh happens during the 166 hours of the week in which readings are n being recorded. We have used Meteorological records to help assess the average outside conditions during the year (4).

Table 1 shows the Meteorological (Met) Office readings Acklington, which is 16 miles North East of Wallington, a Nation Trust propery in Northumbria. It can be seen that the readings 0900 and 1500 have a significantly higher temperature and low relative humidity than the 24 hour average. Therefore the readings that are recorded at the houses can be expected to lower than the average.

	0900 & 1500			Full 24 hours			T=Ta+
	AMCa g/kg	Ta C	RHa %	AMCa g/kg	Ta C	RHa %	RH %
January	4.2	3.5	86	4.1	3.2	87	60
February	4.0	3.5	81	3.9	2.9	83	59
March	4.4	5.6	76	4.3	4.4	80	58
April	5.1	8.1	75	5.0	6.5	82	59
May	6.1	10.9	75	5.9	9.2	82	59
June	7.7	14.4	75	7.5	12.5	82	-
July	8.1	15.0	76	8.0	13.3	83	-
August	8.5	15.2	79	8.2	13.4	85	-
September	7.9	13.9	80	7.6	12.4	85	-
October	6.7	10.9	82	6.4	9.8	86	60
November	4.9	5.9	85	4.8	5.4	87	61
December	4.2	3.4	85	4.1	3.1	86	60

Table 1

Throughout the British Isles, Met Office records show that extern average relative humidity is between 70-90%. See Fig 2. With the houses we can expect these values to be affected by the amou of heating, solar gain and damp penetration. Very few of t houses have domestic or even museum levels of heating during t winter and therefore tend to be damp. A high average relati humidity will show up on the spot reading graphs, particular during the winter when the 0900 and 1500 readings are close to t 24 hour average. The graphs can be deceptive when the readings a satisfactory at 0900 and 1500 but go out of specification in t middle of the day and during the night. (See Section 2.3).

2.2 Thermohygrograph readings

Thermohygrographs (5) have been installed at a few properties which particular climatic problems have been identified. They ha been used with most success in houses with enthusiastic housesta who can dedicate the time to maintain the machines.

Figs 3a and 3b show traces from a thermohygrograph installed in t Chapel at Cliveden; the problems and solution of environment control in this building will be described in detail in Secti 3.3. A dehumidifier was installed to try to reduce the relati humidity to acceptable levels. The sawtooth form of both t temperature and the RH traces in Fig 3b is characteristic of environment in which a dehumidifier is in control; the sma regular rise and fall in both values corresponds to the machi switching on and off on the humidistat control.

2.3 Electronic recording and processing

Solid state memory temperature and RH recorders were introduc into the houses in 1985. They have the major advantage of needi no attention by the housestaff. The information that has bee collected by them has already proved its value by helping to gai control of environmental conditions in several properties. At th moment 20 houses are equipped with these intruments and as mone becomes available more houses are buying them.

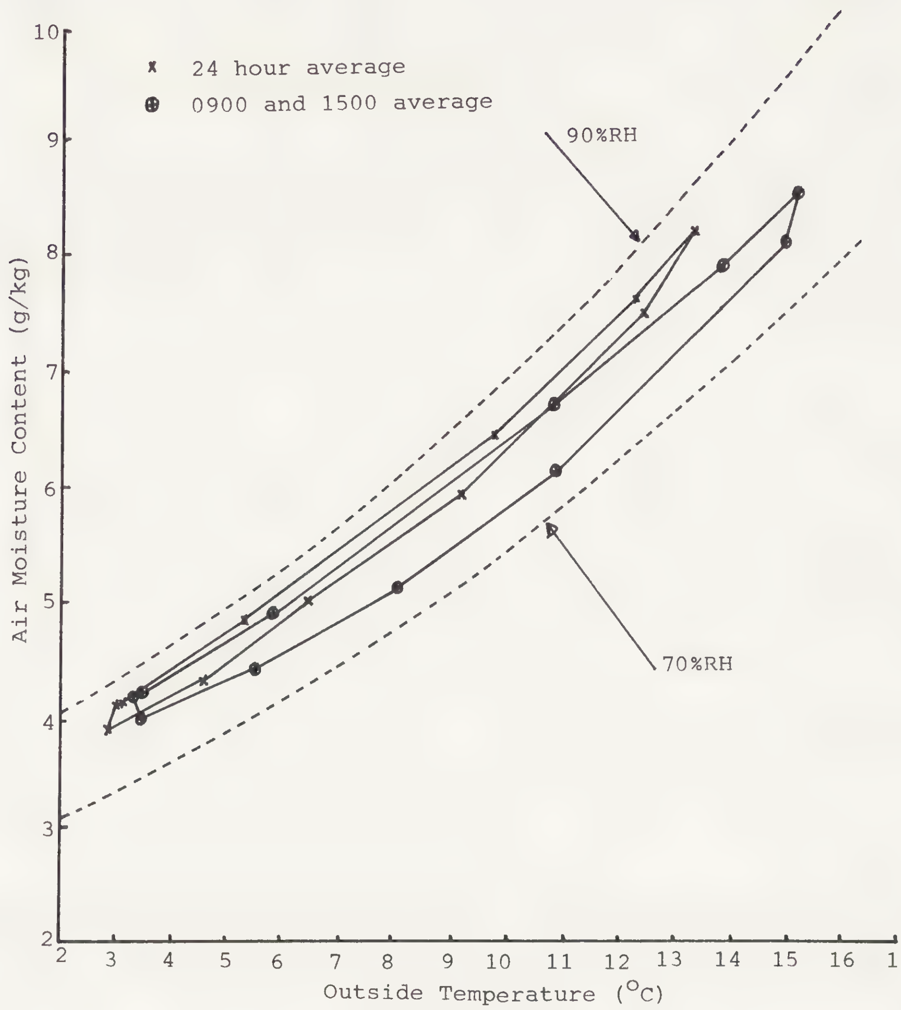

Figure 2 Monthly average values of air moisture content plotted against outside temperature at Acklington, Northumbria (Met Office data 1961-70)

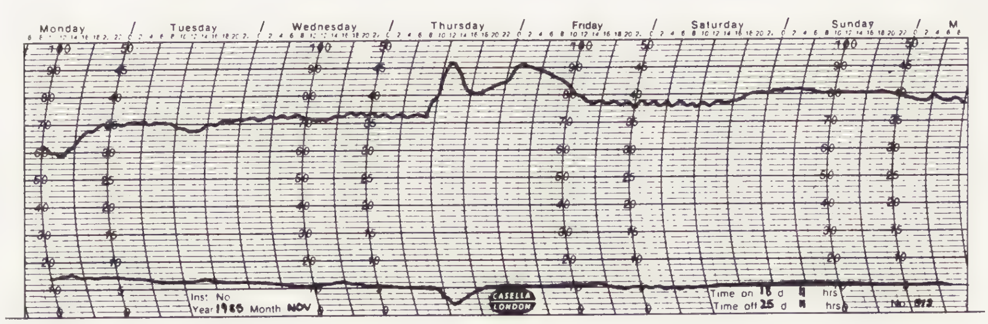

Figure 3a Thermohygrograph trace for typical week in Cliveden Chapel before draughtproofing

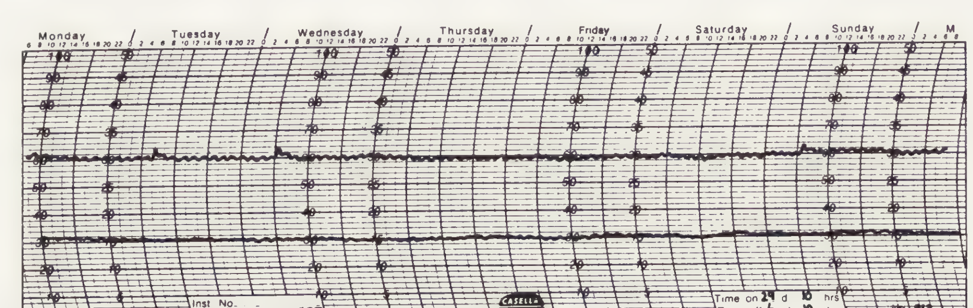

Figure 3b Thermohygrograph trace for typical week in Cliveden Chapel after draughtproofing

Kingston Lacy April-July 1986

Recorder Number 7126

Start: 18th April 1986 15:11:00
Finish: 2nd July 1986 12:11:00

Recording interval: 00:30:00

Number of channels: 4
Readings per channel 3595

Channel 1 statistics

Channel 1 - Temperature - Mini thermistor
Range: -10.00 to 40.00 C
Min: 12.40C 22nd April 1986 04:11:00
Max: 24.60C 28th June 1986 15:41:00
Mean: 17.60C

Standard deviation 2.40C

Other information: Library, bookcase

Channel 2 statistics

Channel 2 - Temperature - Mini thermistor
Range: -10.00 to 40.00 C
Min: 11.80C 22nd April 1986 04:11:00
Max: 23.60C 28th June 1986 15:41:00
Mean: 17.20C

Standard deviation: 2.00C

Other information: Drawing Room, chair

Channel 3 statistics

Channel 3 - Humidity - Capacitive probe
Range: 0.0 to 100.0%
Min 44.0% 18th April 1986 15:41:00
Max: 74.5% 3rd June 1986 13:41:00
Mean: 58.5%

Standard deviation 4.5%

Other information: Library, bookcase

Channel 4 statistics

Channel 4 - Humidity - Capacitive probe
Range: 0.0 to 100.0%
Min: 45.5% 21st April 1986 17:41:00
Max: 75.5% 16th June 1986 13:11:00
Mean: 59.0%

Standard deviation: 5.5%

Other information: Drawing Room, chair

Table 2

Print-out of statistics from Squirrel in Library at Kingston Lacy, April - July 1986

We are using Squirrel meter/loggers (6). These loggers can colle up to 16K readings on four channels, two of temperature and two RH. Recording intervals can be set between one second and nine nine minutes. We usually record every half hour or hour. T logger is powered by a 9 volt battery, which lasts for about s months. If the recorder is set to record every half hour t memory is full in three months; a recording once an hour fills t memory in six months. During this time the recorder needs attention, although it can be used as a meter or can display t readings in memory on a liquid crystal display, without affecti the recording. The temperature sensors we use are thermistors wi a range of -10 to 40°C, the humidity sensors are Vaisala Humicap So far we have found that the calibration has remained within t specified ±2%. The sensors can be used with extension leads up 25 metres long, enabling recordings to be made at locations up 50 metres apart.

The readings are extracted from the recorders in one of two way Either a member of the Conservation Department goes to the hou and loads the data into an Epson HX20 portable computer (7), or t recorder is disconnected from the sensor leads and posted to one the authors. There the readings are processed using an IBM PC (8 As well as taking readings directly from a Squirrel logger, t Epson computer can offload the readings into the IBM. Commerci software is available (6) for processing the results and printi graphs. We have found the options offered in the software adequa for our needs, but plan to extend it to calculate and plot valu of air moisture content.

Table 2 shows a print-out of information about a recording a statistical analysis of the data. Fig 4 is a plot of th temperature and RH in the library at Kingston Lacy, for the sa period as is illustrated in the spot readings in Fig 1. It interesting to note how misleading the spot readings are; almos all are within the range 50-65%RH. However, the 24 hour trace fr the Squirrel logger shows rapidly changing temperature and relativ humidity. The daily temperature cycle is almost certainly cause by solar gain as the Library faces south, the RH changes are mor complex and probably reflect external changes in RH as well as th changing temperatures effect on RH; the house was open to th public for most of this period.

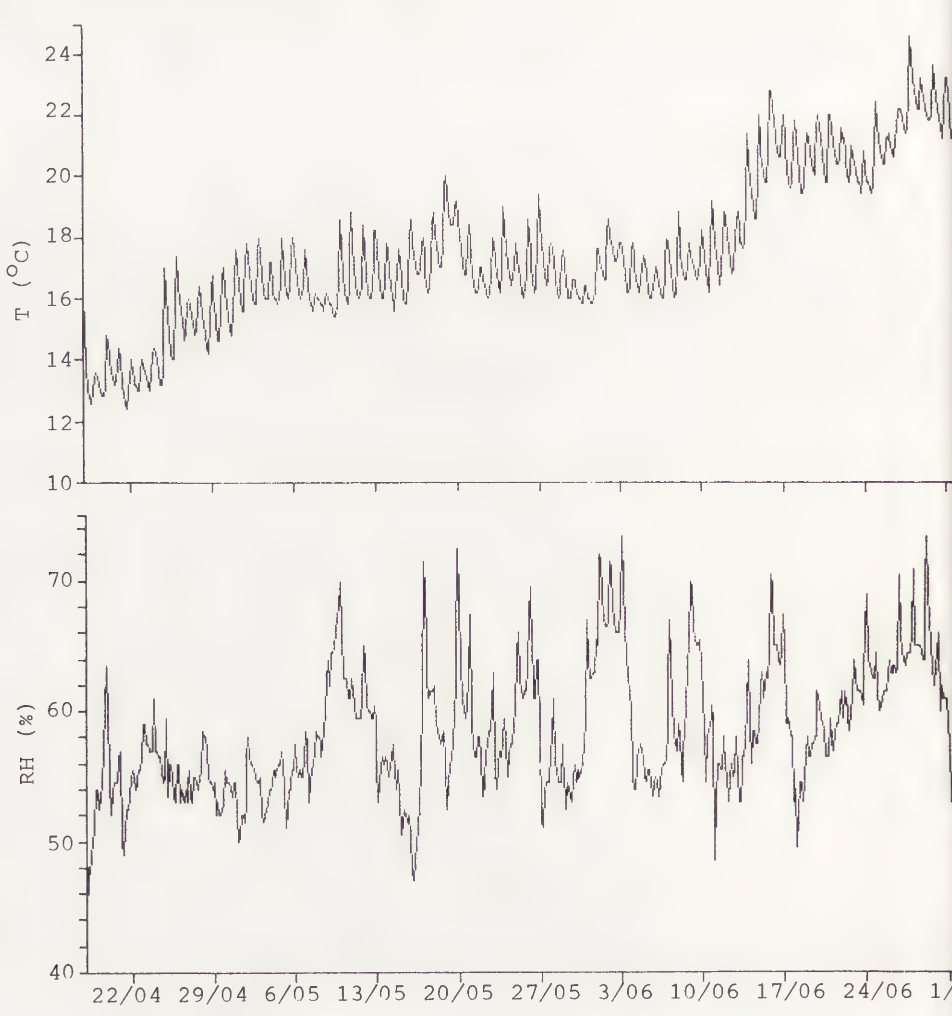

Figure 4

Temperature and relative humidity in Library at Kingston Lacy, April - July 1986. Recorded by Squirrel solid-state memory meter-logger

3. Direct control of relative humidity

Where there is no requirement to provide warmth for people in winter, it is useful to consider direct RH control by dehumidification. As almost all of the National Trust houses are closed to the public from the end of September to the beginning of April, and the majority are unlived in, except for the staff and family apartments, there are extensive areas where the high cost of heating can be avoided.

A study carried out in the Parlour at Monk's House near Lewes in 1984 (9) showed that dehumidifiers can achieve the same measure of RH reduction as heating, using as little as one fifth of the energy input, provided that the space can be made relatively draughtproof (say one air change per hour).

The three examples described below are taken from the many locations where direct RH limitation is a sufficient solution. The alternative, that of increasing indoor temperature in winter to bring the damagingly high external levels of RH down to below the 65% 'mould threshold', is discussed in Section 4.

3.1 Case Study 1 - Calke Abbey Riding School

Calke Abbey came to the Trust in 1985. It is a mansion with over 100 rooms, many of which were filled with furniture, artefacts and collections of all kinds and periods, and including every material. The house was heated by coal fires every winter day until 1924, and this will have maintained reasonable conservation conditions. Since then rising costs and decreasing occupation of the building have resulted in deterioration of the fabric and contents. The condition of the building was such that the entire contents had to be removed to store, while a 3 year restoration programme is carried out, and the indoor environment is improved. The contents must be kept safe and be prepared for their return to the house.

Some space was found in nearby properties - e.g. attic rooms at Sudbury Hall, but the greater part had to be accommodated at Calke. It was decided to use packing cases, typically 1.5 x 2 x 2 metres, for as many of the objects as possible, and to store these in an indoor Riding School within the stable complex. The School measures 12 x 29 metres on plan, and has a free height of 5 metres.

A monitoring programme was started in autumn 1985 using thermohygrographs and Squirrel loggers, measuring T and RH continuously in the house, the Riding School, in packing cases and outside. At the same time it was decided that the more environmentally sensitive and important objects should be concentrated in some fifteen packing cases. An RH-controlled 'tent' was created for this purpose, and the intention was to expand this in a modular fashion to other groups of cases, depending on the initial monitoring results.

The 'tent' was made by fixing Polythene sheets over a scaffolding and timber batten frame, to enclose a volume 6 x 10.5 x 5 metres. A door big enough to admit a case on a fork lift truck was included. Two quite modest refrigerative dehumidifiers (10), with a condensing capacity of 3 litres a day each at 10C and 80%RH, were installed.

This arrangement was successful, with RH in the tent being reduced to 55% over a six week period and then held constant within about 2%. Beyond the Polythene the values varied up to 95% with a mean level of over 80%. Figs 5a and 5b show T and RH traces in the tent and outside it in the Riding School during the first month of the 'drying out' period. Analysis of the monitoring results and the quantity of water collected by the machines indicates that the rate of air leakage through the tent is less than one change per two hours.

One modification to the dehumidifiers was necessary. As these are refrigerative-type machines, they tend to ice up in cold weather. Below about 5°C the automatic defrost cycle does not clear the condensing coil, and the thickness of ice on it can continue to grow until it eventually forms a solid block and stops the machine working. The additional heat required to prevent this is only some 50W, so it was supplied by fitting tubular electric 'greenhouse' heaters next to the cold coils. These were plugged in via a frost-stat set at just over 5C. The machine continued to operate through the cold spell in February 1986, when outside temperatures did not rise about freezing for three weeks and those in the tent fell below zero on ocasion. The heaters increased power consumption but only to a total of 11 KW a day even when they were on all the time. Since the machines operate as heat pumps, they give out a small but important amount of heat. The recordings show that they maintained a differential of about 1.5°C in the tent over the

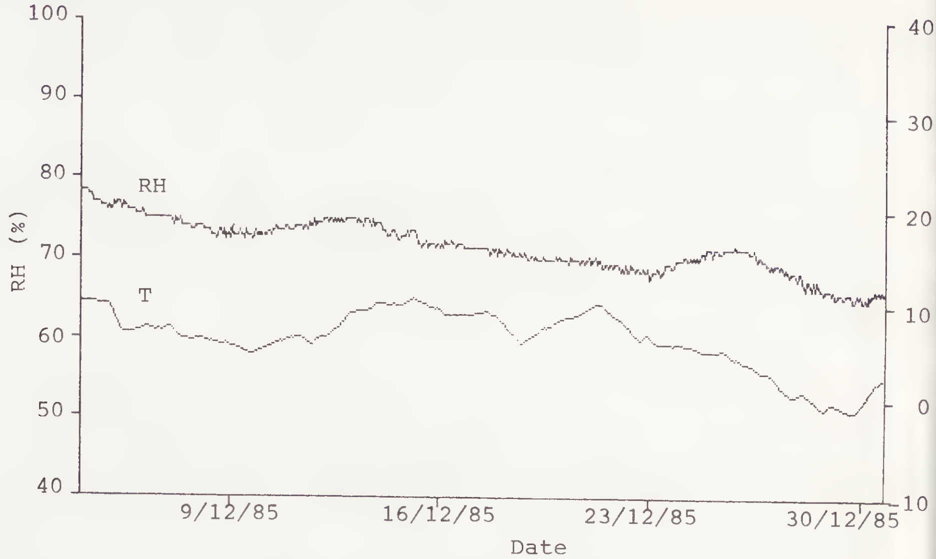

Figure 5a Temperature and relative humidity inside packing ca
in 'tent' in Calke Abbey Riding School

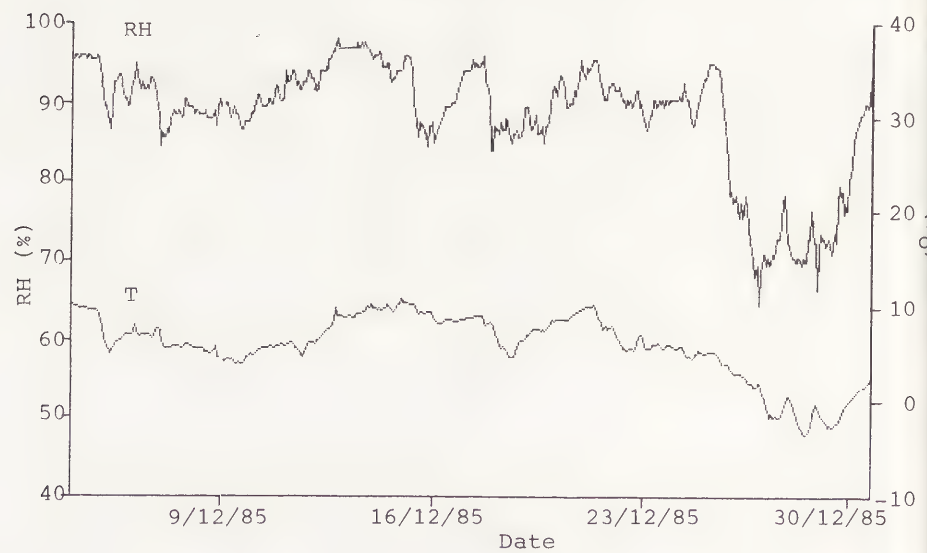

Figure 5b Temperature and relative humidity outside 'tent' i
Calke Abbey Riding School

Riding School at large, and the recorded minima were -2.6°C ther
against -4.6C beyond the Polythene and -8.6°C outside. Refriger
ative machines were used rather than absorption types because i
these instances the former are more energy-efficient even when use
in conjunction with the small amount of heating, for the same rat
of water extraction. They are cheaper to buy, and are available i
a wider range of sizes.

As an experiment one of the dehumidifiers was fitted with a mask o
the output side, so that the dried and warmed air could be fed vi
trunking to pass through a packing case containing metalwork. Th
traces in Figs 6a and 6b show that a useful differential of som
7%RH was maintained by channelling part of the dehumidicatio
effort through the case in this way, without reducing the effect i
the tent, as a whole.

The first winter's results were reviewed in the Spring, and it wa
decided that an improvement should be made in the remainder of th
Riding School for the following year. Draughtproofing work ha
been carried out, and additional machines have been installed
This time both refrigerant and absorption types are being used
Monitoring results, and information on the comparative performanc
of the different machines, will be published in due course.

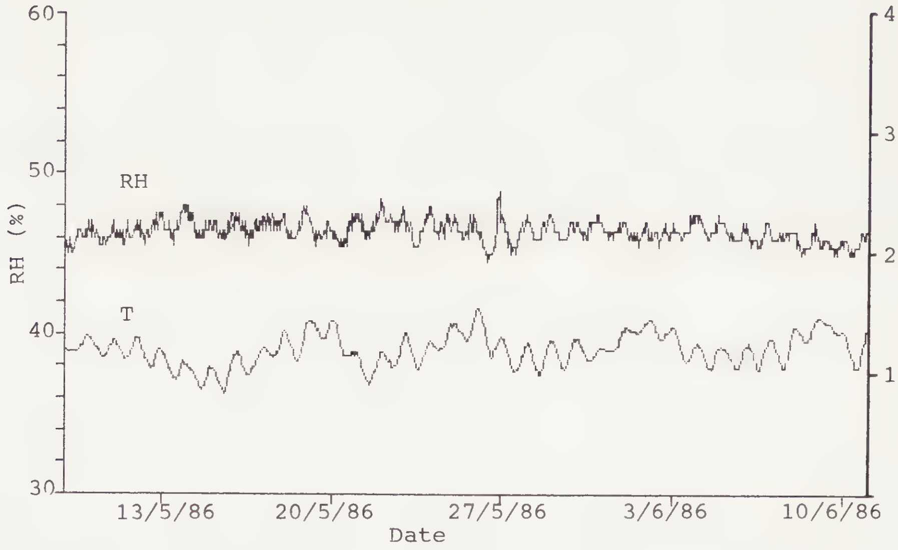

Figure 6a Temperature and relative humidity inside packing case containing metalwork in 'tent' in Calke Abbey Riding School

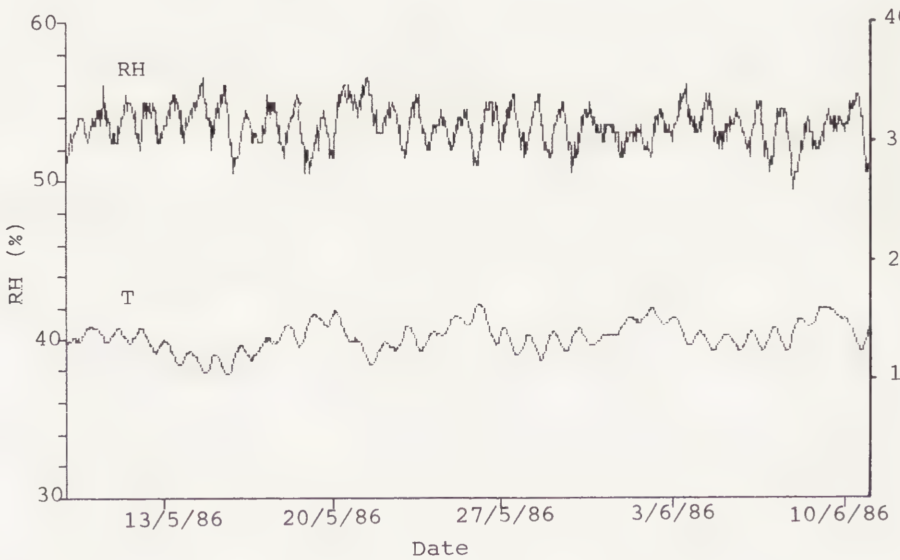

Figure 6b Temperature and relative humidity in 'tent' in Calke Abbey Riding School

3.2 Case Study 2 - Canons Ashby 'Green Cloth'

A large silk embroidery of the arms of William III on green baize hangs on the south wall of the Hall at Canons Ashby in its original silvered picture frame. Conditions in the Hall are not yet controlled, and the house suffers damp penetration through the cellars, artifically increasing air moisture content and RH. A display case has been made to reduce atmospheric pollution and improve the buffering of ambient climatic changes for the cloth. It is recognised, however, that provision of a airtight case is not sufficient, indeed mould growth may be encouraged by the lack of air movement. Unless the temperature of the winter air inside is increased or its air moisture content, reduced, the average RH level will remain about 65% most of the time. The use of silica gel was considered but the quantity involved (for a volume of $1.2m^3$) was substantial and the problems of handling it in and out of the display case and reconditioning it in this country house were daunting.

In principle the most attractive solution to the problem is to dry the air with a dehumidifier. No record was found of a similar venture, though there are references dealing with total museum style installations with humidification and air drying (11). An experimental set up was therefore commissioned to develop and demonstrate the technique.

In its simplest form the scheme was to run inlet and exhaust ai pipes from the display case to the cellar beneath, completing closed circuit with a dehumidifier. The machine would be switche by a humidstat in the case, to pump in dry air whenever the R there rose about 65%. Filters could be introduced to ensure ai cleanliness, and it was thought that a tube of silica gel might b useful in the circuit to smooth out sharp RH cycles as the machin switched on, defrosted etc.

In practice there were problems, arising from the difficulty o finding a humidistat with a small enough switching differential and the unsuitable behaviour of the dehumidifier when the air flo through it was reduced to the gentle rate required. All th standard machines available had their cold and warm coil physically close together. At low airflows the heat generated i the compressor side of the circuit soon influenced the cold coil reducing or preventing condensation of the water vapour from th air. The RH of the outgoing air was still reduced by virtue of it rise in temperature, but this advantage was short lived when i reached the case, as it quickly cooled again.

The dehumidifier was therefore installed in a 1.2 x 1.2 x 1.5 metr Polythene 'tent' built on a timber batten frame, to create reservoir of dry air from which a supply to the display case coul be taken when necessary. Initially the machine was left to operat on its internal humidistat, but again the rise in air temperatur proved a problem. In order to allow for the increase in RH as i cooled again, a level of 35-40% was needed in the tent. Without a expensive high-specification humidistat this involved the machin running for considerable lengths of time, increasing the hea output still further. Examination of T and RH readings taken i the tent at intervals of a few seconds showed that the heatin effect was insignificant for the first 2-3 minutes of operation while condensation started within half a minute. A timer wa therefore introduced in place of the humidistat, to run the machin for 2 minutes every 12 minutes.

Since the temperature in the cellar at Canons Ashby falls below 5C icing up of the dehumidifier must be prevented. Models with a lo wattage heater fitted inside the cold coil are now produced, i response to these and similar problems. One of these (9) was used As supplied the heater must be switched on and off, but thermostat was fitted in the circuit (set at 10C) to do thi automatically. This heater has to perform the full duty of de-frosting the cold coil, as the machine's built in mechanism i seldom triggered when power is only supplied for 2 minutes at time. The arrangements had the desired effect, producing reasonably constant RH in the tent of 45-50% with only a degree o so rise in temperature. Ice build-up was prevented even when th temperature fell to near zero.

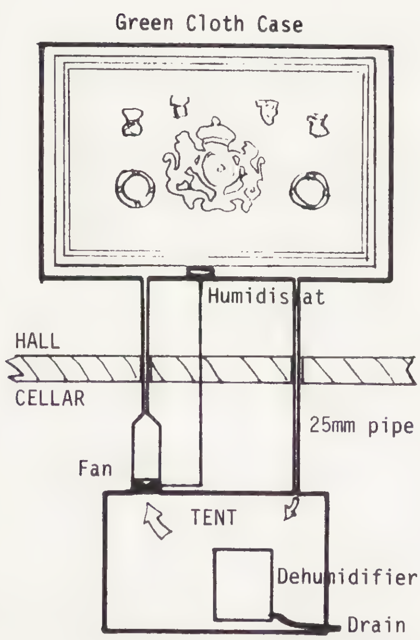

Figure 7

Diagram of set-up for control of RH inside case for green cloth at Canons Ashby

The final problem was to tap this reservoir of dry air and pump i into the Green Cloth case. A standard 100mm diameter axial fan wa fitted to an opening in the wall of the tent blowing into a 0.5m length of 100mm pipe to allow the main turbulence to die awa before reducing to the 25mm pipe to the case. This fan is switche by a hair humidistat with a constant temperature switchin differential of 1.5% RH, located in the display case (a plasti barrel for these tests). Fig 7 is a diagram of the set-up and Fi 8 shows that the RH can be kept between 50-60% against an ambien level of 80-90%.

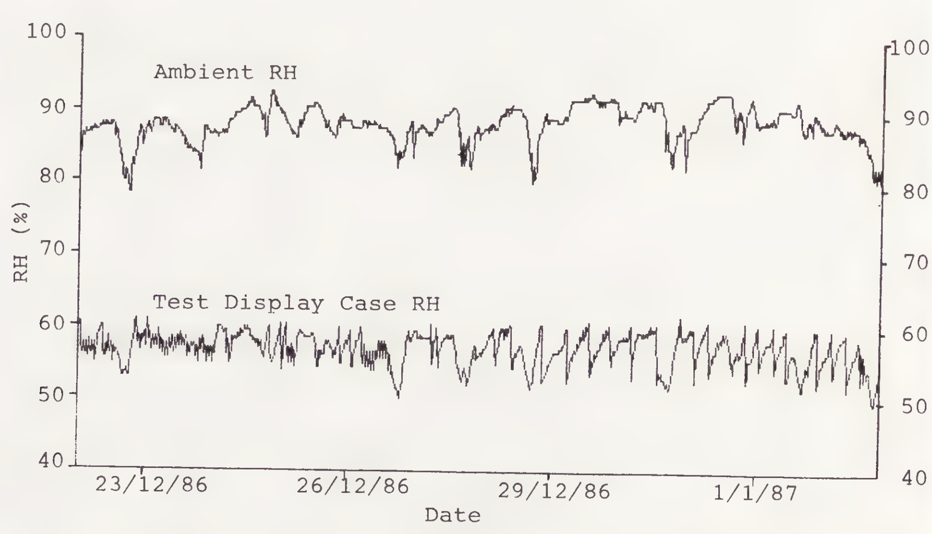

Figure 8

Relative humidity inside test display case compared with ambient conditions during trial for environmentally-controlled case for Canons Ashby Green Cloth

3.3 Case study 3 - Cliveden Chapel

In the garden of Cliveden, home of the Earls of Orkney through the 18th Century, is an Octagon Temple, designed by the Italian architect, Giacomo Leoni, in 1735. After changing hands several times during the 19th Century, the house was bought by William Waldorf (later 1st Viscount) Astor in 1893. He immediately commissioned J.L. Pearson to convert the Temple into a Chapel, with its walls and dome encrusted with mosaics by Clayton and Bell. The 1st Viscount and many other members of the Astor family have since been buried there.

The Chapel has always suffered water penetration from the chalk bank in which it is set, from rainwater off the roof and paving at Parterre level, and through the floor. A number of these sources of damp have been tackled, but it has not been possible to solve the problem completely. The mosaics and the thin marble and alabaster revetments, which make up the inside surfaces, have been damaged by the passage of this water causing efflorescence of salts and chemical reactions within the sensitive materials. The painted and gilded altar piece has recently undergone conservation work, but will quickly need treatment again if the indoor environment is not controlled.

A dehumidifier was installed in autumn 1985. The machine is capable of dealing with up to two exchanges of air per hour with the outside, and no additional draughtproofing was carried out at that time. Temperature and relative humidity were monitored with a thermohygrograph. While it was evident from the monitoring that the dehumidifier had been useful in reducing RH, its effectiveness was intermittent and not as positive as expected for a room of this size. Several features of the record indicated that draughts were the problem. There was no clear differential in air moisture content inside and out, and there appeared to be no buffering effect due to the building's fabric.

The traces in Fig 3a are from this initial operating period. The dehumidifier had control of the atmosphere some of the time, demonstrated by the characteristic 'saw-tooth' trace produced as the humidistat turns the machine on and off. However, it lost control for long periods. Even allowing for an instrument calibration error of 10%RH, the room level reached 82% when the set value was 60%.

A site inspection was carried out, and a number of points noted. For example, the latch on the heavy bronze door had about 6mm play. Although the door closed to the frame under gravity, westerly winds easily pushed it back to the latch limit, allowing a considerable draught. There was also a gap under it in the closed position, even though it scraped the floor as it opened. One of the high level pivoting windows was found to be in need of maintenance as it would not close completely - again leaving a gap of 5-10mm.

The second pair of traces (see Fig 3b) from the Chapel were taken after the door and window has been draughtproofed. The monotonous straight line RH record speaks for itself, and the ripple of the temperature line is evidence that this space is now buffered against rapid external weather cycles by the building's fabric.

This example has been included in order to underline the different approach that is needed if dehumidifiers are to be used successfully in old buildings. Different, that is, from heating. We understand the effect of heat and the ways in which it is dissipated because our bodies are sensitive to changes in temperature, and our pockets to domestic heating costs. The mixture of radiant, conductive and convective heating mechanisms makes our houses tolerant of ventilation, we can for example recover some losses by increasing insulation.

Dehumidifiers operate more simply, they dry the air. As the treated air leaks out and is replaced by new from outside, this in turn must be dried. Of course when room RH is maintained at conservation levels the moisture content of the furniture and contents will gradually fall to a safe level in equilibrium with that value, but the machine must be in control of the atmosphere before this can happen. Also the cost of operating a dehumidifier is directly related to the residual rate of air change - as it is humidistat-controlled it runs only when RH rises above the set value. In the long term, therefore, a high standard of draught-proofing is usually cost-effective.

4. Control of relative humidity through temperature

It is not sufficient, for conservation, to ensure that a buildin is weathertight. If the fabric allows damp to penetrate, then i is true that the removal or neutralisation of that additional caus of high RH, by drying or heating the air, decreases the magnitud of the problem. Even if there is no such extra moisture evaporat ing indoors, however, we still have to improve conditions artifici ally.

Nature's winter mechanisms are highly effective as the trigger an catalyst of decay in preparation for the spring. Outside in the U the mean RH level is 85-90% right through the colder months. It i of course the same air with the same absolute moisture content in doors, even if extreme cyclic values are attenuated to some exten by a slow rate of leakage in well-maintained buildings. Indoor R will only be lower than ambient if the temperature is highe (ignoring for the moment direct reduction of air moisture conten by dehumidification).

A few metres underground the temperature is constant all year roun at about 7°C, in equilibrium with the gradual release of heat fro below and the average of the seasonal variations above. The shel of a substantial building insulates it to a degree, and keeps th inside in slightly closer contact with the body of the eart beneath. However, it is only in underground caves and perhaps som deep basements that the winter temperature cycle has no effect.

In summer solar gain ensures that our buildings remain a fe degrees above ambient temperature, and this is usually sufficien to reduce RH from a 24 hour average level of 75-80% to aroun 60-65% indoors. As winter progresses the natural differentia between inside and outside temperatures gradually falls, and i most buildings it is no more than one or two degrees for fou months or more. Indoor RH is then over 70% nearly all the time.

Table 1 is taken from Meteorological Office records from 1961-197 at an inland continuous recording station (Acklington). Averag monthly values of ambient moisture content, temperature and RH ar given. The last column shows the effect of raising the temperatur 5C above those levels during the winter heating season. The clea implication is that, on average, we can create reasonab conservation conditions in winter by providing this level o background heat.

Fig 9 includes two years of winter spot readings (See Section 2.) taken outside at Wallington, plotted on a graph of air moistur content against outside temperature. The Table 1 values are als shown, together with the area within which indoor RH will b between 50% and 65% if a constant differential of 5°C is maintain over ambient. This demonstrates not only that the monthly mea values are comfortably centralised in this 'conservation' band, bu also that it encompasses the great majority of the more scatter spot readings.

It is most advantageous from the point of view of heating syste capacity and running costs that the 5°C temperature differentia required is low and constant. As heat input is proportional to th temperature increment, 'conservation heating' systems may need onl a quarter of the capacity of that for domestic comfort (typicall to produce 20°C at 0°C outside). This also means that the emitte can be quite unobtrusive, indeed historic radiator layouts ar often capable of doing this job.

Control of conservation systems can conveniently be arranged usin a proprietory weather-compensating controller. This is a devic with two inputs, one of outside temperature and the other o circuit flow temperature, which can be programmed to maintain linear relationship between the two. This tuning process i necessarily empirical as it depends on the particular therma chacteristics of the building. It can be achieved by monitorin temperature and relative humidity inside and out through successiv controller setting adjustments, refining the gradient and offset o the flow/ambient temperature line, until the result is acceptab throughout the range of winter conditions.

In most of the Trust's properties the complete solution involves second more positive level of control in some important rooms o showcases. Paradoxically this can be cheaper than the backgroun heating, for example if RH control by dehumidification is feasible Nevertheless the cost of general background heating is normall justified because the houses are visited daily even in the close season by staff, conservators, cleaners, tradesmen etc.

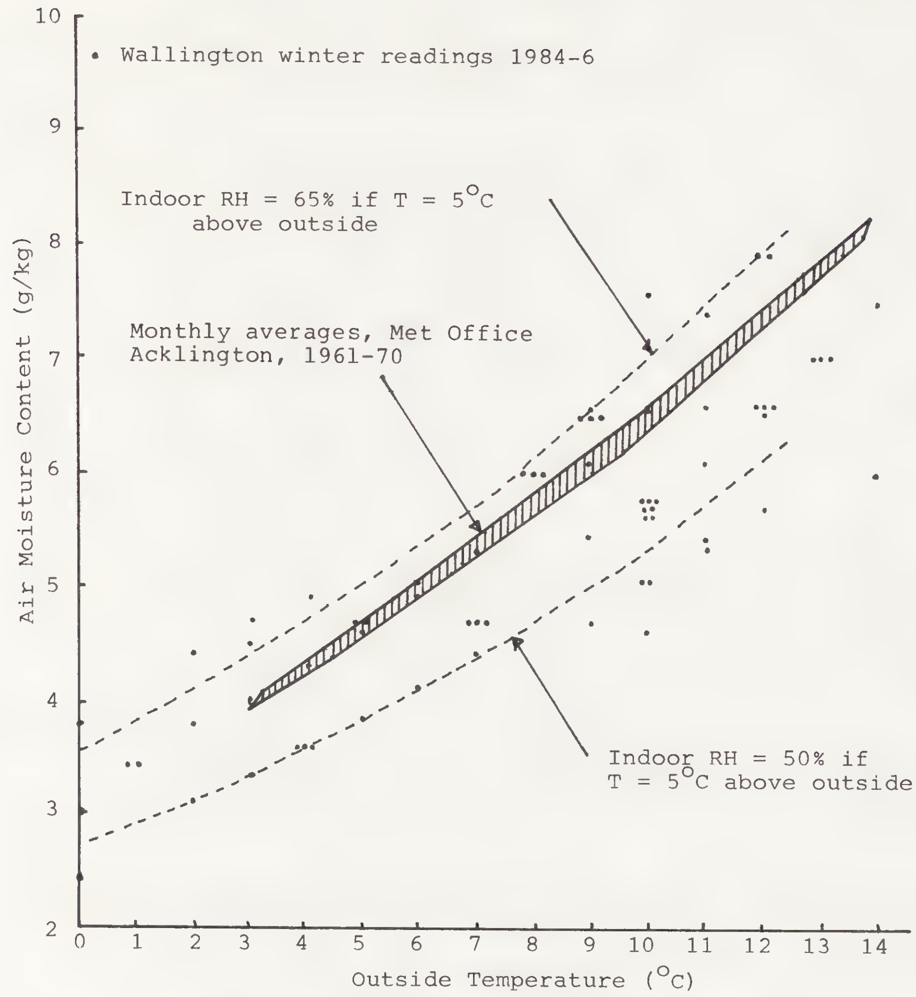

Figure 9 Two years of winter spot readings at Wallington plotted on graph of air moisture content against outside temperature

Aesthetic constraints on changes to the fabric of National Trust houses mean that it is seldom possible to bring thermal or air-sealing characteristics up the standards of a modern building. Thus in general it is not feasible to provide the same degree of environmental control for the contents as in a purpose-built museum. However it is usually possible to arrange the relatively low level of heating needed to achieve the above modest increase in temperature, and this is the design target adopted for a first level of indoor atmospheric control.

The Government's Department of Energy currently operate an Energy Efficiency scheme for non-domestic (largely industrial) premises. They have agreed that surveys to review environmental control for conservation in historic houses which open to the public and which recommend energy-efficient improvements to plant, controls, instrumentation etc. qualify for grant assistance under this scheme. The National Trust has derived considerable benefit to date, from thirty initial Short Surveys (12) and six Extended Surveys, where the need for more detailed investigations or monitored trials has been identified.

5. Conclusion and future plans

The examples used in this paper are drawn from many projects taking place in National Trust houses. We hope they are representive of the type of work that we have undertaken to date. This is a relatively new field for the National Trust and we have many candidates for attention which we hope to report at future meetings.

One technique which are are interesting in developing is the use of humidistats to control heating systems. This has already been reported by a member of the Working Group at a previous meeting (13). We have found that the switching differentials of the majority of humidistats is so great, and the thermal inertia of the majority of the heating systems in our houses so massive (that is,

the power of the heating system is not sufficient to respond to th relatively rapid changes in humidity that may be encountered in draughty building) that we have not employed them so far. However in small scale projects, such as the Clive Museum at Powis Castle in which one room is being prepared for the exhibition of collection of items brought back by Clive from India, we intend t experiment with the use of humidistatic control of the radiators.

There can be no doubt that with 200 houses in the care of th National Trust, there will be interesting projects to be tackle for many years to come.

6. Notes and references

1. 'The National Trust Manual of Housekeeping', compiled Hermione Sandwith and Sheila Stainton. Allen Lane, London, 1984.

2. Whirling hygrometer T8716/1 (with British Standard 28 thermometers, temperature range -5 to 50C) from Casella London Lt Regent House, Britannia Walk, London N1 7ND. Telephone 01 253 858

3. Novasina MIK 3000-C (with capacitive sensor) from Humite Peter Greaves & Associates Ltd, PO Box 30, Horsham, West Susse RH13 6DE. Telephone 0403 730 730.

4. Climatological memorandum No.103. August 1976. Meteorologic Office, London.

5. Thermohygrograph T 9186 (ranges 0-50C and 0-100%RH) fr Casella London, Ltd., Regent House, Britannia Walk, London, N1 7N Telephone 01 253 8581.

6. Squirrel meter/logger SQ16 2U/2L, Epson HX20 Standard Analys Program, IBM PC Standard Analysis Program all from Gra Instruments (Cambridge) Ltd., Barrington, Cambridge, CB2 5Q Telephone 0763 60811. Cost approximately £1000 for logger wi pair of temperature and humidity sensors.

7. Epson HX-20 portable computer and RAM expansion unit availab from computer retailers, or complete with RAM expansion unit a program on EPROM from the Grant Insturments (Cambridge) Ltd., Barrington, Cambridge, CB2 5QZ. Telephone 0763 60811.

8. IBM PC available from computer retailers. Grant Analys Program will also run on IBM compatible computers such as Olivet M24, Ferranti PC860 and Zenith Z150.

9. Bob Hayes, 'Monk's House,Rodmell - a case study in atmospher humidity control using a dehumidifier - Extended energy surv report' Internal National Trust document, March 1985.

10. Dryfast Major and Dryfast Major low temperature version fr Selectair Ltd. Becketts Wharf, Lower Teddington Road, Hampton Wic Kingston-on-Thames, Surrey, KT1 4ER. Telephone 01 943 4144.

11. Michalski, S., 'A control module for relative humidity display cases'. Preprints of the IIC Washington Congress September 1982, London, 1982. Pp. 28-31.

12. Bob Hayes, 'Wallington - Environmental Control, Short surv report'. Internal National Trust document, August 1986.

13. Lafontaine, R.H. and Michalski, S., 'The control of relati humidity - recent developments'. Preprints of the 7th trienni meeting of the ICOM Committee for Conservation, Copenhagen, September, 1984. 84/17/33-37.

UMMARY

t the Handicraft Museum of inland a humidification ystem with ventilation ppliances was introduced in 984 and used for one year. uring this time there was o technical problems but he humidifiers of this type ere found out to be a evere health risk. The cold ater which these appara- uses use favours the growth f bacteria and fungus. here seems to be no way to eep the system clean enough. nstead of the ventilation nd nebulazation appliances he safe method is to use he steam humidification ystem, in which water is lways heated enough to revent all bacteriological rowth.

PROBLEMS WITH THE HUMIDIFICATION SYSTEM AT THE HANDICRAFT MUSEUM OF FINLAND

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Introduction

The Handicraft Museum of Finland was reopened to the public in Jyväskylä, Central Finland, in 1983. It functions as the national museum of handicraft in Finland. The Museum is housed in what used to be the Public Library of Jyväskylä, a building which had previously served as a granary. The granary was constructed in 1851 and was converted into a library in 1915. When the building was converted into a museum in 1981-1982, its original appearance of around 1910 was preserved as far as possible. The renovation was carried out observing a modern museum's needs as concerns office space, fire and theft protection, lighting and quality of exhibition cases.

The Museum occupies a total area of c. 1000 m^2. The museum building proper comprises three exhibition halls, offices, archives, a library, service facilities and storage space for textiles and other collections. A conservation laboratory and more office space are situated in two adjacent buildings. The three exhibition halls are in two storeys linked by open passages and staircases, the total exhibition space being 270 m^2.

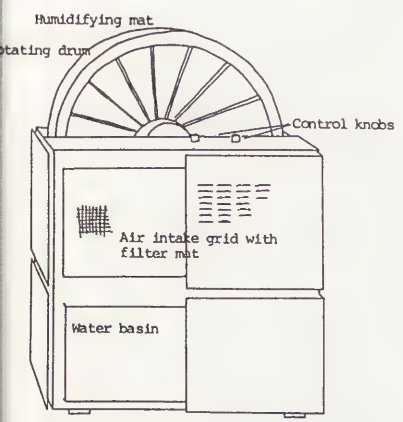
Because of the cold climate, relative humidity indoors in Finland in winter time often falls below 20%, since no humid air gets in when the temperature outdoors falls to +3°C. This means that in Finland, for most of the year, airing or other means of ventilation does not improve the dry air indoors. Too dry air causes health problems by furthering the spreading of influenza or exacerbating the symptoms of allergy. Humidification is needed because it has been found out that in 30-60% R.H. the reproduction of many bacteria is diminished. Virus causing inflammation in respiratory passages die the easiest in 50-70% R.H. High enough humidity levels are thus needed not only for the important well-being of museum collections but also for that of the museum staff. Yet too high humidity can cause serious symptoms of allergy. Furthermore, if relative humidity can be raised up to 40-60% in winter, the temperature can be lowered by a few degrees. This saving of energy is economically important.

The great differences in winter and summer temperatures (from -25°C to +25°C) have an effect on the temperature and humidity conditions inside buildings even if air conditioning is being used. In winter relative humidity can be kept at about 40 $\pm$ 5%, temperature +20 $\pm$ 2°C. In summer it may be possible to maintain 50 $\pm$ 5% R.H., temperature +24 $\pm$ 2°C.

If in winter relative humidity has to be raised above 50%, there is a risk of condensation on all cold walls and window surfaces since the difference in temperatures inside/outside can be over 30°C. If for some reason a 60% R.H. in large scale is needed in winter months, a room-in-room show case must be built which is separated from the structures of the building.

Humidification System

During the renovation work at the Handicraft Museum of Finland a humidification system was to be installed. As no central unit was planned, the system had to be chosen from the small, individually operating appliances, which are either of the ventilation type, the nebulization type or the steaming type. The first one was selected as in the literature it was recommended for museums.



ig. 1: Construction of the efensor 2000-V and 2000-VA.

A Defensor 2000-V or 2000-VA operates on the ventilation principle. The dry room air is forced by a fan through a dry and a wet filter. The air is filtered before it reaches the fan, then humidified and forced through a filter. The humidifying mat, which is the wet filter, is clamped onto a rotating drum and thoroughly wetted in the water basin. Lime and impurities in the water are held back in the appliance. Moistured air is ejected into the room from the top of the appliance. The built-in hygrostat automatically controls the required humidity. Figure 1.

Three Defensor 2000-VA humidifiers were placed in the exhibition halls. One of them was installed in the hall for the Museum's basic exhibition (100 m^2), the other two in the rooms for tempo-

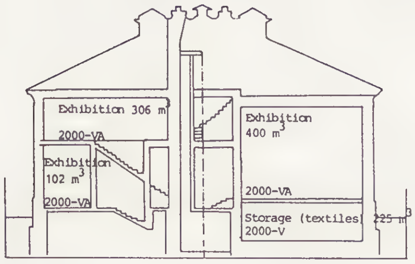


Fig. 2: The locations of the humidifiers in the Museum.

rary exhibitions, one of the rooms being two flights up. One Defensor 2000-V with handfilling was installed in the textile storage space (90 m^2). The 2000-VA's were automatically supplied with unfiltered tap water, which in Jyväskylä is soft, about 3°dH. The other model was filled with deionised water. It was not possible to have any kind of device in the storage space of other collections because the building work was not completed. Figure 2.

The system started running in September 1984. The register for February 1985, which was cold, shows that one device was sufficient to keep R.H. above 40% in the room for the basic exhibition. In August 1985, relative humidity was high, but the humidifier had to be kept working to level down fluctuations in humidity, which otherwise would have been rather sharp. Figure 3.

The third humidifier, which was placed on the top floor, was used only at a low rate, if at all, since the upstairs humidity seemed to be affected by that of the other rooms. In warm summer days the air in this room was humid and stuffy in a somewhat unpleasant way. The exhaust fan did not help much.

There were no technical problems with the humidifiers during the 12-month-long operating time. Automatism functioned well and no leakages occurred whereas the cleaning of them proved to be time-consuming and later also problematic and expensive. A thorough maintenance of one humidifier took nearly two hours for one person. So for the four machines almost one full working day was needed.

At first, cleaning was done once a month according to the instructions given by the importer. Maintenance includes

- removing movable parts
- cleaning air filters
- removing lime deposits
- cleaning micro-organic slime.

The water basin and air filters were washed together with the humidifying mat, which was replaced if necessary. Lukewarm water and mild detergents were supposed to be enough for cleaning but from the very beginning mild disinfectants were used for washing the humidifiers. Lime deposits on the drum were removed both by scraping them away and by using a de-liming detergent. To keep the water pure Micropur water purification tablets were used, at first two tablets per two weeks.

Problems

Within about six months it was realised that cleaning done at four-week intervals was not enough. Each time the humidifiers seemed to be more and more slimy. Now they were cleaned every

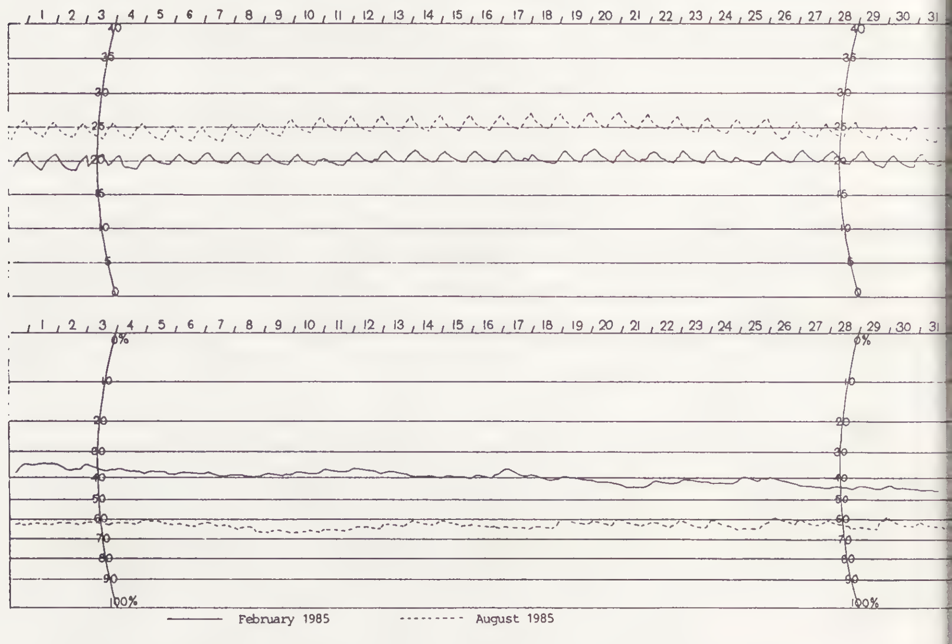


Fig. 3: Thermohygrograph recordings in the hall for the Museum's basic exhibition.

fortnight and the expensive humidifying mats were replaced once a month. The supplier told us that at least four Micropur tablets should be used for each two-week interval. After having received a recommendation we also tested the use, instead of tablets, of a silverion plate, which was supposed to be more effective and more economical. One silver plate is active for almost a year until it has dissolved totally. We had such a plate in one water basin for about three months. Later, in that particular device, microbiological growth was by visual estimate not so wild as it was in the others.

Early in the autumn of 1985, after the system had been running for 12 months, we realised that it was not possible to keep the humidifiers clean. Although stronger disinfectants were used as soon as one week after cleaning, there was a very visible growth of micro-organisms and a very strong and bad smell spreading around. This happened with the humidifiers which were filled with tap water. Defensor 2000-V with deionised water and located alone in the textile storage space had all the time stayed almost clean without any noticeable slime. This was again judged only visually, and no specific examination or tests were done.

At this point, after the situation had turned really bad, none of the appliances was used any more, and the Museum contacted the Health Authorities. The recommendation given was that we should not use humidifiers of the ventilation type because of the severe health risks which they cause. Both ventilation and nebulization humidifiers use cold backwater, and the low temperature of about +10°C favours bacteriological growth. This very abundant growth of bacteria and fungus is spread by humidity and inhaled into the lungs. In hospitals where ventilation humidification has been in use, neither cleaning with strong disinfective solutions nor the use of ultraviolet rays to kill bacteria in the water basin of a central machinery has proved to be effective enough. We did not try UV-rays on our small appliances in the Museum.

In some large offices and manufacturing establishments with a similar central humidification system with ventilation machinery there have been reports of what is called humidifier fever: symptoms similar to those of influenza, which get worse during workdays but ease out during weekends and holidays. The most serious cases have developed into asthma and caused a permanent incapacity for work.

Conclusion

The only safe and recommendable method of humidification was told to be a system using a steaming appliance in which water is always heated to +65°C, which prevents all bacteriological growth. Cleaning simply means getting rid of lime deposits, which in some apparatuses can be done half automatically. An additional advantage is also silent operating without draft.

In the Handicraft Museum of Finland a central system of steam humidification will be introduced in 1987. In the show rooms an Ufox Steamatic Electronic will be installed. In the storage area it is not possible to build ducts, and thus small individual steam humidifiers will be introduced. New ducts in the public area are also problematic and have to be built gradually to reach appropriate efficiency with minimum intervention. The adaptation of an old building to museum use causes various problems when modern museum technology should be implemented.

Importers

Defensor 2000-V and 2000-VA humidifiers,
Defensor Micropur water preservation tablets:
Ekström, PL 41, 02101 Espoo, Finland

Ufox Steamatic Electronic humidifier:
Ufox oy, 41800 Korpilahti, Finland

IMMARY

is paper describes the thod of lighting control dopted for the public ex-bition of the mural aintings in Fahai Temple, eijing. In particular, the thod by which ultraviolet adiation was filtered using uorescent lamps fitted th an AC-1 type UV-absorbng film is described. In ddition, this article gives brief account of earlier ethods designed to filter ltraviolet radiation and elates these to the latest esearch of our institute, owing the properties of e AC-1 type film.

DEVELOPMENT OF A UV-ABSORBING FILTER IN CHINA AND ITS APPLICATION TO THE PROTECTION OF THE MURAL PAINTINGS OF FAHAI TEMPLE, BEIJING

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1. A Brief Description of the Mural Paintings in Fahai Temple

The Fahai Temple is in Moshikou Village, at the southern foot of Cuiweishan mountain, in the western suburbs of Beijing. Built between 1439 and 1443, the temple was constructed for the imperial family in the Ming Dynasty.

For over 500 years Fahai Temple has experienced many vicissitudes of the ages. The entire original structure no longer exists, with only the main hall remaining. At present more than 200 square meters of fine Ming Dynasty mural paintings are preserved in the main hall. For a long time the paintings were not open to the public. This was primarily because the problem of preventing damage by light (especially ultraviolet radiation) was not solved. For this reason the main hall was closed for many years, and the mural paintings were preserved in dark conditions throughout this period.

The mural paintings in the temple were made with extra care. Their artistic level is fairly high and it is assumed that the paintings were executed by talented craftsmen of the imperial court. The mural paintings were made by first spreading thick plaster on to the temple's solid walls of brick. The paintings were then painted on to this layer of plaster. So far no air pockets between the plaster and the brick have been discovered and neither has flaking of the paint occurred. There are a few old cracks, however,but these do not appear to have influenced the overall stability of the mural paintings.

A front and back door exist in the main hall which houses the mural paintings. As a rule the back door is not open and all the doors and windows have been screened by black curtains. When the doors are closed, the mural paintings are preserved in dark conditions. This is a great advantage for the preservation of the colours of the mural paintings since fading cannot occur. Because the main hall is on the highest position in the temple, air can circulate comparatively well and the relative humidity level is not too high throughout most of the year. These are also important factors why the mural paintings are so well preserved.

In recent years, with the development of tourism in China and a more open foreign policy, there has been a growing desire by foreign visitors to see the fine Ming Dynasty mural paintings within Fahai Temple. In order to satisfy the demands of the public to solve the problem of how to exhibit the mural paintings safely, our institute carried out some research. The work investigated the types of light sources which might be used to exhibit the mural paintings to the public and, in particular, how the ultraviolet radiation emitted from these sources could be absorbed in order that damage to the paintings would not occur.

2. Early Methods of Filtering Ultraviolet Radiation

An early and simple method of removing ultraviolet radiation was the application of zinc white or titanium white paint to the surfaces within museums. Light reflected from these surfaces contained less ultraviolet radiation but it was not removed completely. When it was commonly known that normal window glass absorbs ultraviolet radiation below a wavelength of 300 nm, research focused on methods of filtering ultraviolet radiation between wavelengths of 300 and 400 nm. Early work designed to produce special glasses which could absorb ultraviolet radiation between these wavelengths experienced difficulties. The technological processes necessary to produce the glasses were complicated. Extreme corrosion occurred in the manufacturing process, and the process was also known to be harmful to human health. Furthermore, the cost of production was expensive and the glasses' effectiveness in eliminating ultraviolet radiation was not good.

In the early 1970's, discussions on these types of problems were held between our institute and other organizations such as the Beijing Institute of Glasses and the Beijing General Factory of Glasses. Everyone agreed that research to develop special glasses would not be worthwhile. With advances in science and technology at that time, materials known as ultraviolet absorbates were discovered. Ultraviolet absorbates can selectively absorb ultraviolet high-energy photons which are harmful to high molecular weight polymers. They act to transform the energy of ultraviolet high-energy photons into thermal energy or second class radiation energy (fluorescent energy) which are harmless to the polymers.

During this period we conducted some experiments designed to dissolve the ultraviolet absorbate into a synthetic resin, which was then coated to the surfaces of window glasses. The coatings which were produced effectively filtered the ultraviolet radiation but they failed to adhere firmly to glasses or other films. It was found that the coatings could split or peel off easily. In addition, these coatings have a lustre and their transparency is not very good.

In 1978 our institute successfully produced a trial product made from a new kind of organic glass which could filter out ultraviolet radiation. The organic glass, which has a thickness of 18 mm, can be made into boxes for the preservation of vulnerable antiquities. Its drawback is that it is more cumbersome to make, and its production cost is expensive.

After March 1980, we began to develop a kind of transparent ultraviolet-absorbing film in which is dissolved an ultraviolet absorbate. The film is made of cellulose tri-acetate, which contains the ultraviolet absorbate. The product is known as AC-1 type ultraviolet-absorbing film. It has a thickness of 0.1 mm. The film transmits visible light very well but its transmission of ultraviolet radiation is very low- close to zero.

The ultraviolet-absorbing film overcomes the weaknesses of coatings since it is a firm whole which is not easily ruptured. It is very durable and it costs less to produce this kind of film. In addition, the method by which it is applied is simple and convenient. The film is covered over the fluorescent lamp which is used. In addition, it can be adhered to the back of a window pane or placed between a double-layered window pane if natural lighting is used for exhibition illumination. Since ultraviolet rays are filtered out no matter how it is used, it is therefore suitable for use with both natural lighting and artificial light sources.

3. Properties of the AC-1 Type Ultraviolet-Absorbing Film

a) Spectral Properties

The transmission of ultraviolet radiation (wavelengths of 200-400 nm) is less than 0.01%, while the transmission of visible radiation (wavelengths of 400-760 nm) is more than 95%. A report prepared by the Sensitized Chemistry Institute of the Chinese Academy of Sciences indicated that the AC-1 type film possesses a strong absorbing capacity between wavelengths of 280 and 380 nm, in which the transmission of ultraviolet radiation is zero. Figure 1 illustrates the good UV-absorbing capacity that these films have.

When the film was tested with a UV Monitor Type 760 (made by Littlemore Scientific Engineering Company in England), the reading was well less than 50 microwatts/lumen, the lowest graduation on the instrument. (The allowable value for museum use is 75 microwatts/lumen or less.)

b) Stability (resistance to light)

i) The film was put on a 40 watt fluorescent lamp which was illuminated for 6720 hours. After this period the film was tested and it was found that there was no change in transmission between the ultraviolet and visible regions of the electromagnetic spectrum. Although slight changes in the film's absorbance of light were noted, the optical density was more than 2. This showed that the film's UV-absorbing property did not change. Thus it can be considered that the film is durable (see Figure 2).

ii) After the UV-absorbing film was adhered to the back of a window pane and exposed to the sun for more than four years, it was found that the film's UV-absorbing capacity had not changed.

In addition, its absorbance of light had not changed, and transmission of both visible and ultraviolet regions of the electromagnetic spectrum had not altered (see Figure 3).

4. Use of the AC-1 Type Film for the Exhibition of the Mural Paintings in Fahai Temple, and the Method of Lighting Control for the Exhibition of the Mural Paintings to the Public

As previously discussed, AC-1 type film can filter UV-radiation emitted from either daylight or artificial light sources. For the exhibition of the mural paintings in Fahai Temple to the public, we choose to use an artificial light source which had a UV-radiation filter. We felt this method was more safe and dependable. To carry out this, the thirty 40 Watt fluorescent lamps installed in the main hall were covered with the AC-1 type UV-absorbing film. The fluorescent lamps were arranged into two equal groups, in which every other lamp was connected to one on-off switch, and the remaining fifteen lamps in the other group were connected to another on-off switch. This produced two separate banks of artificial light, which enabled us to control the illumination according to the number of light sources required. From this one is able to control the illumination from the light sources for the preservation of the mural paintings.

All of the doors and windows in the main hall where the mural paintings are exhibited were covered with curtains made of black cloth. All of the main hall, occupying an area of 242 square metres, is therefore illuminated only by artificial light, which has been filtered to eliminate UV-radiation.

In May 1985, after the artificial light sources had been in use, we selected ten representative points in the main hall in order to test to the emission of ultraviolet radiation from the sources. Using a UV Monitor, it was found that all the values were less than 50 microwatts/lumen, all close to zero.

With respect to controlling the illumination from the light sources, we have tried to restrict the level of intensity of the artificial lighting as much as possible. The number of lamps which are used to provide illumination is controlled in order that the illumination remains within the limits of 50-100 lux. In addition, the lamps are turned off when there are no visitors in the main hall, and the time period which is allowed to illuminate the mural paintings for the public is shortened as much as possible.

The mural paintings in the main hall have been on exhibition ever since the Fahai Temple was opened to the public.
However, in order to limit the number of visitors to the temple, we have decided to charge them to cover the cost of the services which are now provided. In addition, we have been very careful in controlling the time which the visitors are allowed to view the mural paintings.

Since the mural paintings in Fahai Temple were opened to the public more than a year ago, the colours of the paintings are still dazzingly beautiful, having the appearance of the original colours. Fortunately, up to now no new problems have been discovered.

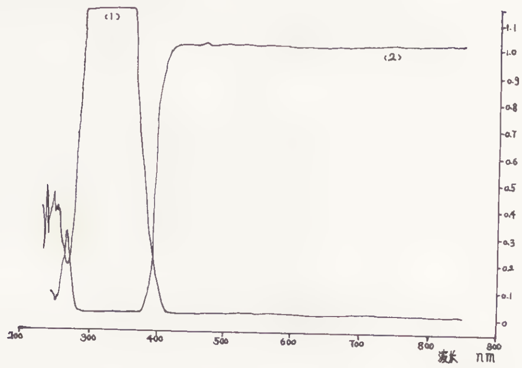

Fig. 1. The absorption spectra of AC-1 type UV-absorbing film.
(1). optical density-- wavelength (optical density times 3).
(2). transmittancy-- wavelength

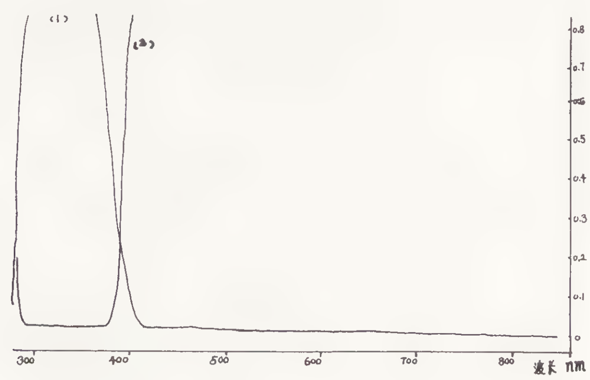

Fig. 2. The absorption spectra of AC-1 type UV-absorbing film after it was put on a 40W fluorescent lamp which was illuminated for 6720 hours.
(1). optical density-- wavelength (optical density times 3).
(2). transmittancy-- wavelength

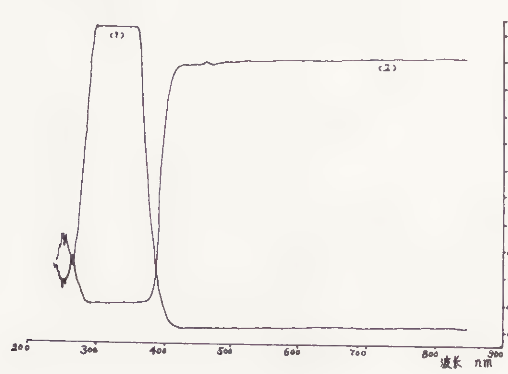

Fig. 3. The absorption spectra of AC-1 type UV-absorbing film after it was adhered to the back of the window-pane to expose to the sun for more than four years.
(1). optical density-- wavelength (optical density times 3).
(2). transmittancy-- wavelength

Working Group 18

Conservation of Leathercraft and Related Objects

Conservation des cuirs artisanaux et objets similaires

TRIENNIAL OVERVIEW
CONSERVATION OF LEATHERCRAFT AND RELATED OBJECTS.

EMBERS

.A. Barlow Haningsberg (Canada)
h. Calnan (UK)
. Chahine (France)
. Fenn (Canada)
. Göpfrich (W.Germany)
. Hallebeek (The Netherlands)
. Hanssen (The Netherlands)
. Howatt-Krahn (Canada)
. Herskovitz (USA)
. Horton (USA)
.U. Johansson (Sweden)
. Komejan (Canada)
. Kroupa (USA)
. McCrady (USA)
.K. Mills Reid (W.Australia)
. Morishita (Japan)
h. Newton (Canada)
. Odekirk (USA)
.E. Peacock (Norway)
. Raphael (USA)
.L. Rose (USA)
. Szalay (Hungary)
. Schaffer (Canada)
.L. Schmidt (Denmark)
. Schmitzer (W.Germany)
. Schulz-Buchanan (Australia)
. Segal (Canada)
. van Soest (The Netherlands)
. Starling (UK)
. Sturman (USA)

Coordinator
T. Stambolov
(The Netherlands)

PROGRAMME 1984 - 1987

1. To promote responsible conservation of leathercraft products and artistic and archaeological objects of leather as well as other objects through communication among the members.

2. To encourage the exchange of experimental findings or other relevent information providing this does not interfere with the sovereignity of a particular work or with the priority reserved for the publishing of this finding.

3. To examine the merits of available methods and to develop new ones in matters concerning the salvage of dray, pulverising archaeological leather decay, in particular the red rot.

4. To study the conditioning of leatherwork with respect to exposition and storage.

5. To refine the formulations employed in the treatment of decaying leather.

6. To assess existing training programmes and to stimulate their development by propagating them as as well as by translating the instructions on which they are based into various languages.

An overview of activities

A symposium on the "Conservation of ethnographic and water-logged leather" was held on June 9, 10 and 11, 1986 in Amsterdam with the purpose of clarifying some yet unattended problematic subjects.

In the course of the symposium, objects made of human skin were dealt with extensively. Ethnographic, as well as archaeological leahter objects, were given attention in due proportion.

Tattooing was reviewed from the anthropological and contemporary standpoints, and the collection of tattooed human skin on display at the Medical Museum in Tokyo was commented upon in view of the conservation treatment practiced there.

Human skins used for bookbinding were the subject of another lecture, in which structural differences between human and other skins were shown and their identification explained.

The conservation and restoration of leather objects from archaeogical sites or regained from the sea were discussed at length, and so were old Eskimo kayaks, 16th century garments, and gilt leather on exhibition in Holland, Japan, and elsewhere.
Fishskins and other untanned hides, received due attention, and the difficulties in removing hazardous insecticides used to disinfect leather objects in museums in the past, were reported in view of the growing concern with the conservator's safety.

The proceedings of the symposium are available (write to: Central Research Laboratory, P.O. Box 5132, 1007 AC Amsterdam, The Netherlands).
The next symposium is planned to take place in 1988, at the German Leather Museum in Offenbach/Main, Germany.

Up-to-date information concerning all aspects of the safeguarding of leather objects has periodically been disseminated through "Leather Conservation News", a bi-annual journal published by the Materials Conservation Laboratory, Texas Memorial Museum in affiliation with this working group (write to: LCN, Material Conservation Lab. BRC 122, 10100 Burnet Rd. Austin, TX 78758 USA).

In order to stimulate the exchange of experimental findings and other knowledge among parties interested in the field of leather conservation, several internships were organized and completed.
They were conducted at conservation institutes and workshops in Europe.

Research needed to clarify matters as indicated in the programme, has been continued -and in some neglected areas, as for instance overzealous conservation, even initiated- along the following lines:

. Checking the consequences due to excessive oiling in the past.
. Understanding the diffusion pattern of polymeric consolidants in the leather texture.
. Developing methods for the determination of the fat content in small samples.
. Identifying the various vegetable tanning materials in archaeological leather.

ESUME

uand on est en présence de cuir chéologique, il s'agit le plus uvent de cuir gorgé d'eau, ayant journé sous terre et recouvert de mbreuses souillures. Le nettoyage pour but d'éliminer les résidus de rre, les particules métalliques (fer incipalement) et les concrétions lcaires. Si les premiers ne sistent pas à un lavage avec une lution détergente, les impuretés étalliques et calcaires nécessitent ntervention de traitements imiques.
ne étude portant sur l'efficacité et nnocuité de différentes substances oposées pour le nettoyage des irs archéologiques a été treprise afin de déterminer les éthodes les plus appropriées. Nous rons ainsi retenu un surfactif non nique et un ampholyte pour le ttoyage superficiel et le citrate ammonium pour la complexation fer.

NETTOYAGE DES CUIRS ARCHEOLOGIQUES GORGES D'EAU

Claire Chahine et Léon-Bavi Vilmont

Centre de Recherches sur la Conservation des Documents Graphiques
36 rue Geoffroy-Saint-Hilaire, 75005 Paris, France

Les milieux humides, dépourvus d'oxygène, sont favorables à la conservation du cuir ; cependant, l'état dans lequel on le retrouve dépend de divers facteurs, en particulier pH du sol (les sols acides sont les plus favorables), microorganismes présents, degré de tannage et niveau d'usure au moment de l'enfouissement. C'est le cuir de tannage végétal qui résiste le mieux à ce type d'environnement.

Les cuirs exhumés sont très sales, recouverts superficiellement de résidus de terre ; ils peuvent également présenter des particules métalliques et des concrétions calcaires plus profondément incrustées. La première étape de la conservation consiste donc à nettoyer ces cuirs dans un but tout d'abord muséologique, afin qu'ils soient présentables, mais aussi pour les rendre aptes à l'étude, en supprimant tout ce qui pourrait masquer des détails, comme les trous de couture ou autres impressions ; enfin le nettoyage vise à débarrasser le cuir des substances qui pourraient se montrer nocives dans le temps, en particulier les particules métalliques, susceptibles de catalyser des réactions d'oxydation. Après leur exhumation en effet, les cuirs sont soumis à des agressions provoquées par l'oxygène de l'air ambiant, les mauvaises conditions thermohygrométriques, les polluants atmosphériques.

Nous avons relevé dans la littérature spécialisée des substances proposées pour le nettoyage des cuirs archéologiques et nous en avons testé l'efficacité, d'une part visuellement sur un lot de cuir mis à notre disposition, d'autre part à l'aide de la spectrométrie de rayons X à dispersion d'énergie pour ce qui est des complexants du fer. Enfin, l'enthalpimétrie différentielle à balayage (DSC) nous a permis à la fois de suivre l'élimination de ces produits du cuir et de détecter d'éventuelles dégradations.

Principe du nettoyage

Il consiste à extraire du cuir les souillures déposées à la surface pendant l'enfouissement. On doit commencer par brosser soigneusement les objets sous l'eau courante. Si ce traitement s'avère insuffisant, l'utilisation de détergents devient alors nécessaire ; ceux-ci sont des surfactifs qui agissent en émulsionnant la saleté.

Les surfactifs (2) sont des composés dont la molécule renferme une partie lipophile et une partie hydrophile ; ce sont des électrolytes et leur classification est basée sur le sens de leur ionisation en solution aqueuse. On distingue ainsi :
- les non ioniques qui ne présentent pas de dissociation ionique
- les anioniques dans lesquels la chaîne lipophile se trouve du côté de l'anion (comme les savons $R\text{-}CO_2^-Na^+$)
- les cationiques (qui sont essentiellement des dérivés d'ammonium quaternaire) dans lesquels la longue chaîne se trouve du côté du cation
- les ampholytes qui renferment des groupes acides et aminés qui s'ionisent en un sens anionique ou cationique atténué suivant le pH.

Les non ioniques et les anioniques sont des détergents. Les cationiques présentent deux propriétés spécifiques : un pouvoir désinfectant important et une affinité pour les fibres naturelles leur communiquant une souplesse et un toucher agréable (désigné sous le nom "d'adoucissage en textile") ; ils n'ont pas de propriétés détergentes mais peuvent être associés à des surfactifs non ioniques. Les ampholytes ont un pouvoir détergent communiqué par leur caractère anionique et un pouvoir bactéricide dû à leur caractère cationique.

Le cuir peut également contenir des impuretés métalliques provenant de l'environnement dans lequel il était placé ; bien que favorables à une bonne conservation pendant l'enfouissement, elles sont susceptibles de dégrader le matériau après l'exhumation en catalysant des réactions d'oxydation. Pour débarrasser le cuir de ces impuretés, il est possible d'utiliser divers agents complexants conduisant à la formation de composés solubles dans l'eau.

Quant aux concrétions calcaires souvent incrustées de façon tenace, il n'est pas toujours aisé de les déloger par action mécanique et il est nécessaire de faire appel à l'action d'acides forts ou encore d'agents complexants. Ces sels calcaires n'étant pas dangereux pour le cuir, leur élimination est uniquement un problème d'esthétique ; ajoutons que dans certains cas l'opération peut améliorer la flexibilité du matériau.

Efficacité des traitements

1. Détergents
Nous avons expérimenté un détergent non ionique, l'Arkopal N 100 de Hoechst (éther polyglycolique de nonylphénol), un détergent anionique, le dodécylsulfate de sodium (SDS) et un détergent ampholyte, la Tégobétaïne de Colgate-Palmolive (diméthylbétaïne en C_{12}-C_{14}). nous avons délibérément écarté les savons qui ont une faible stabilité en eaux dures. Ces expériences ont été menées sur un lot de cuir du 17e siècle provenant d'un chantier de fouilles du Nord de la France, Tourcoing. Après rinçage et brossage à l'eau courante, les cuirs sont placés dans une solution à 10 % de détergents sous agitation pendant trois heures. Les ultra-sons peuvent améliorer la qualité du nettoyage mais, ayant observé une dégradation mécanique nette sur certaines structures affaiblies, nous avons préféré ne pas les utiliser. Les cuirs sont ensuite rincés à l'eau

courante. L'efficacité a été appréciée de façon visuelle et nous avons retenu l'Arkopal N 100 et la Tégobétaïne. Nous avons ajouté à la solution de détergent 0,5 % de carboxyméthylcellulose afin d'empêcher la saleté de se redéposer sur les fibres (5).

2. Complexants du fer
Dans les cuirs archéologiques, le fer se trouve essentiellement sous forme d'oxydes hydratés (Fe_2O_3, nH_2O), de sulfures, de tannates ; ils peuvent également être fixés sur la fibre de collagène.

Ne disposant pas de cuir archéologique contenant des impuretés métalliques, nous avons tenté de reproduire les conditions de ce type de matériau à partir de cuir neuf, où seuls les facteurs fer-collagène, fer-tanin ont été pris en compte. A cet effet, des échantillons de cuir tanné végétalement ont été soumis à l'action du mélange eau-acétone (50/50) qui provoque la solubilisation des tanins non fixés, des non-tanins et des graisses, dans le but de favoriser la pénétration des traitements ultérieurs ; puis on y a introduit Fe^{+++} sous forme de chlorure ferrique à 1 % ; les cuirs ainsi traités ont ensuite été soigneusement rincés à l'eau courante pendant 24 heures.

Expérimentation
Nous avons examiné l'efficacité des composés suivants : sel disodique de l'EDTA à 5 % (Ethylène Diamine Tétracétique Acide), pH 4,5, en 2, 4, 5 et 12 heures ; citrate d'ammonium 2 et 5 % en 2, 4 et 12 heures ; acide citrique 3 et 5 % en 2 et 4 heures ; acide oxalique 1, 3 et 5 % en 1/2, 2 et 4 heures ; hexamétaphosphate de sodium 1 et 5 % en 2 et 12 heures ; Coriagen K de Hoechst (polyphosphate acide à chaîne relativement courte utilisé en tannerie pour débarrasser le cuir des taches de fer) à 2 % en 2, 4 et 12 heures ; APDC 1 % (= Ammonium Pyrrolidine Dithio Carbamate) et NaDDC 1 % (= Diéthyl Dithio Carbamate de sodium) 1, 4 et 12 heures, suivis d'une extraction du complexe à l'aide de la méthyl isobutylcétone.
L'expérimentation a été menée sur quatre séries de cuir.

Des analyses élémentaires ont été réalisées en spectrométrie de rayons X à dispersion d'énergie couplée au microscope électronique à balayage*.
L'appareillage utilisé se compose d'un microscope Jeol JSM 35C et d'une sonde Ortec. Les mesures ont été faites à une énergie de 20 keV, après métallisation au carbone, sur le côté chair du cuir dont la structure fibreuse lâche retient plus facilement les composés qui y sont appliqués. La technique ne permet pas de faire des mesures quantitatives, elle donne uniquement la proportion relative des éléments présents.

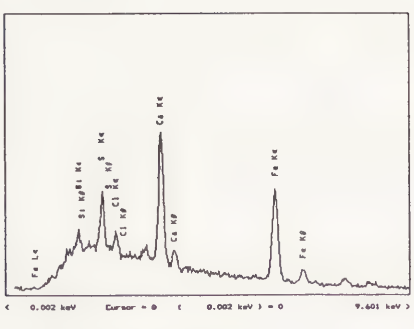

Figure 1 : cuir traité Fe Cl_3 1 %
et rincé 24 heures

Résultats
On constate que le témoin traité au chlorure ferrique contient encore d'assez grandes quantités de fer après rinçage à l'eau (fig. 1) ; cela signifie que le fer s'est fixé chimiquement sur le collagène ou sur le tanin. D'autre part, aucune trace de fer n'a été trouvée dans les blancs, lavés ou non.

Tous les complexants essayés diminuent de façon importante le contenu en fer, mais aucun ne l'élimine complètement. Néanmoins, dans certaines expériences, on ne retrouvait plus de fer, mais ces résultats n'ont pu être confirmés en répétant l'opération, même avec des temps de contact longs.

Quelques composés semblent cependant plus actifs que d'autres, en particulier le coriagen K à 2 %, l'APDC et le citrate d'ammonium à 5 % (fig. 2) ; il est d'ailleurs plus actif que l'acide citrique à la même concentration. Dans un précédent travail, CALNAN (1) avait déjà mis en évidence l'efficacité du citrate d'ammonium pour complexer le fer. Nous ne retiendrons pas le traitement à l'APDC qui laisse des quantités de soufre assez importantes ; d'autre part, le cuir ainsi traité présente une rétraction non négligeable due sans doute à l'emploi de la méthylisobutylcétone.

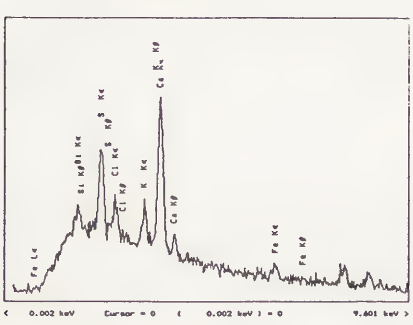

Figure 2 : cuir traité Fe Cl_3 1 %
puis 2 heures citrate d'ammonium 5 %
et rincé 24 heures

M E B: JEOL JSM 35 C
Microsonde ORTEC System 5000
Laboratoire de Géologie du Museum National d'Histoire Naturelle (convention MNHN-CRCDG)

Innocuité des traitements

1. Technique utilisée
L'étude a été réalisée en enthalpimétrie différentielle à balayage (DSC) à l'aide d'un DSC 4 de Perkin-Elmer. Cette technique permet de mesurer la température de dénaturation (T_D) du cuir qui dépend de différents facteurs internes (les liaisons qui stabilisent la molécule et celles qui lient le tanin à celle-ci) mais aussi de facteurs externes, comme la nature du solvant (3-4) ou encore le pH du milieu aqueux (5) dans lesquels on fait la mesure. Une diminution de la température de dénaturation n'est donc pas nécessairement un signe de dégradation due à des ruptures de liaisons dans la molécule, elle devrait être alors corrélée à d'autres tests pour être prise en considération ; la mesure peut également indiquer la présence d'un soluté dans le milieu et donc permettre de suivre son élimination.
L'échantillon, placé avec de l'eau dans une capsule sertie, subit une montée linéaire de température en même temps qu'une référence inerte ; au moment de la dénaturation, un pic proportionnel au flux de chaleur différentiel apparaît sur la courbe de montée en température.

L'analyse par DSC ne nécessitant que de petits prélèvements, nous avons pu travailler sur du cuir archéologique gorgé d'eau, donc dans des conditions réelles ; ainsi l'expérimentation a été menée sur des cuirs médiévaux et des cuirs du 19e siècle.

* Nous tenons à remercier Mme Françoise LECLERC pour l'aide qu'elle nous a apportée dans les analyses par cette technique

Ce type de cuir est très hétérogène et présente une dispersion dans les mesures de thermostabilité selon l'endroit du prélèvement ; afin de pallier cet inconvénient, nous avons travaillé sur de petites éprouvettes en prévoyant un témoin pour chacune d'elles. Dans les tableaux présentés ici, nous ne tiendrons pas compte des modifications de $T_D \leqslant$ 4-5°C.

2. Etude des détergents

Nous avons expérimenté l'effet de l'Arkopal N 100 à 10 %, du SDS à 1 et 10 %, de la Tégobétaïne à 10 % pendant 1 à 3 heures. Le cequartyl (bromure de lauryldiméthylcarbéthoxyammonium) pouvant être ajouté aux solutions de nettoyage pour ses propriétés adoucissantes, nous l'avons testé à 5 et 10 % pendant 3 heures ; d'autre part, il est utilisé pour ses propriétés désinfectantes et nous l'avons donc essayé aux mêmes concentrations mais en un temps plus long, deux semaines ont été choisies arbitrairement. Parallèlement au céquartyl, nous avons examiné un autre sel d'ammonium quaternaire, le Präpagen WKT de Hoechst (chlorure de dialkyldiméthylammonium). Des rinçages à l'eau courante ont été effectués après les traitements.

Résultats

Les résultats sont présentés dans le tableau I. il en ressort que l'Arkopal et la Tégobétaïne ne modifient pas la thermostabilité du cuir ; on constate en outre qu'un rinçage court (une heure) est suffisant. Nous avons observé que le SDS à la concentration de 10 % provoque en 1, 2 et 3 heures une légère diminution de la température de dénaturation d'un cuir médiéval. En répétant la mesure sur un autre cuir de même époque, nous n'avons pas retrouvé le même effet. Ce composé, qui est rupteur de liaisons hydrogène, devrait cependant, à notre avis, être utilisé avec prudence. Nous ne le retiendrons pas, d'autant qu'il n'est pas d'une grande efficacité pour le nettoyage.

Les traitements au céquartyl, s'ils sont courts (3 heures), ne modifient pas ou peu la thermostabilité. Après 2 semaines, on observe que la température de dénaturation (fig. 3) est fortement diminuée, même après un rinçage soigneux qui devrait éliminer toute trace de ce composé. Ce résultat nécessite bien entendu d'être corrélé à celui d'autres tests pour être tout à fait sûr d'un effet délétère, mais il nous semble cependant prudent de ne pas appliquer ce désinfectant au cuir. L'autre sel d'ammonium quaternaire étudié ne semble pas avoir le même effet négatif sur le cuir.

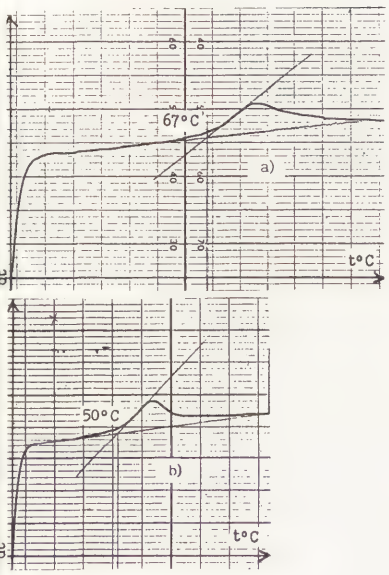

Figure 3 : DSC de cuir archéologique
a) témoin
b) traité 2 semaines cequartyl BE 10 %, rincé 24 heures

3. Etude des complexants du fer

Nous avons testé l'effet de tous les complexants précédemment cités à l'exception de l'APDC qui n'avait pas été retenu. Les temps de contact ont été de 1 à 3 heures et les rinçages effectués à l'eau courante.

Résultats

D'après les résultats du tableau II, on observe des thermostabilités des cuirs traités différentes selon les composés et les valeurs mesurées permettent de tirer quelques conclusions.

L'acide citrique est facilement éliminé du matériau, en deux heures à la concentration de 3 %, en 4 heures maximum à celle de 5 % ; par contre, le citrate d'ammonium nécessite un rinçage plus long, au moins une vingtaine d'heures. Il faut remarquer cependant que laisser du citrate d'ammonium dans le cuir n'est pas nécessairement néfaste pour sa conservation.

On parvient à retirer complètement l'acide oxalique à 5 % en une nuit après un temps de contact court ($\frac{1}{2}$ heure) ; mais si ce temps est prolongé jusqu'à trois heures, l'opération devient difficile, même en 20 heures de rinçage ; dans ce cas l'abaissement de T_D pourrait être dû également à une dégradation.

La facilité avec laquelle on extrait l'EDTA du cuir, semble également fonction du temps de contact : après 3 heures, l'élimination est aisée, après 4 heures elle devient plus délicate, après 12 heures elle est presque impossible ; dans ce dernier cas, on ne peut écarter non plus l'hypothèse d'une détérioration.

On arrive à supprimer l'hexamétaphosphate de sodium du cuir si le rinçage est suffisant, c'est-à-dire une nuit ; de même pour le coriagen K qui, à la concentration de 2 %, nécessite au moins 20 heures de rinçage pour disparaître complètement.

En conclusion, nous donnerons la préférence au citrate d'ammonium.

4. Etude des agents d'élimination des sels calcaires

Les acides précédemment énumérés peuvent avoir cet effet ; nous avons étudié également le comportement du cuir traité à l'acide chlorhydrique à 3 %, à l'acide phosphorique à 3 % et à l'EDTA à 5 % pH 10 (nous avons utilisé le sel disodique en ajustant son pH avec du silicate de sodium). les temps de traitement ont été de 1 à 5 heures et les rinçages effectués à l'eau courante.

Résultats

Les résultats du tableau III mettent en évidence qu'il est possible de faire disparaître du cuir les acides chlorhydrique et phosphorique, en 6 heures de rinçage maximum pour le premier, en plus de 6 heures pour le second ; d'autre part, même un contact prolongé, comme cela a été effectué pour l'acide phosphorique ne modifie pas la thermostabilité du cuir, si le rinçage est suffisant. Il semble par contre plus difficile d'éliminer les alcalins du cuir que les acides puisque le traitement à l'EDTA pH 10, même après un rinçage long, provoque une diminution de la température de dénaturation, celle-ci pouvant aussi être due à une altération du matériau.

Conclusion

Un lavage à l'eau courante en même temps qu'un brossage suivis d'un traitement à l'aide d'une solution de détergents sous action mécanique sont dans la plupart des cas très suffisants pour nettoyer un cuir de façon tout à fait satisfaisante. L'utilisation d'agents d'élimination des particules métalliques ou des sels calcaires, ne devrait intervenir que dans certains cas particuliers. S'il s'agit d'EDTA ou d'acides, il est prudent, d'une part de ne pas trop prolonger les temps de traitement, d'autre part de rincer suffisamment longtemps (jusqu'à 24 heures pour certains), afin d'éliminer toute trace de ces substances qui pourraient se révéler agressives au cours du temps.

Dans notre étude, nous avons retenu deux surfactifs détergents, l'Arkopal N 100 et la Tégobétaïne à 10 %.

Pour ce qui est de l'élimination du fer qu'il semble assez difficile d'obtenir totalement, notre choix se porte sur le citrate d'ammonium à 5 % en 3 ou 4 heures, il est en effet parmi les plus actifs des composés examinés et tout à fait inoffensif pour le cuir. Notre travail sur les complexants se poursuivra cependant, en particulier afin d'affiner les méthodes d'analyse et tenter d'évaluer quantitativement le fer restant.

Les résultats obtenus en DSC avec le céquartyl mettent en évidence que les sels d'ammonium quaternaire, recherchés pour leurs propriétés adoucissantes et désinfectantes devraient être utilisés avec quelque prudence. Nous examinerons cependant d'autres surfactifs cationiques.

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Tableau I

Thermostabilité du cuir traité avec différents surfactifs

Traitements	Cuir médiéval			Cuir du 19e siècle		
	contact	rinçage	ΔT °C	contact	rinçage	ΔT °C
Arkopal N 100 10 %	3 h.	1 h.	- 1			
		4 h.	0			
S D S 1 %	1 h.	1 h.	0			
	2 h.	1 h.	0			
S D S 10 %	1 h.	1 h.	- 5			
(pH = 4,5)	2 h.	1 h.	- 7			
	3 h.	1 h.	- 6 0			
		4 h.	+ 2			
		6 h.	+ 2			
Tégobétaïne 10 %	3 h.	1 h.	- 2			
(pH = 6,5)		4 h.	0			
Céquartyl 5 %	3 h.	24 h.	- 2			
(pH = 5)	2 sem.	1 h.	- 22	2 sem.		
		6 h.	- 16		6 h.	- 15
		24 h.	- 16		24 h.	- 10
Céquartyl 10 %	3 h.	1 h.	- 6			
(pH = 5)		24 h.	- 2			
	2 sem.	1 h.	- 24	2 sem.		
		6 h.	- 19		6 h.	- 12
		24 h.	- 17		24 h.	- 10
Präpagen WKT 10 %	3 h.	1 h.	- 3			
(pH = 6)	2 sem.	24 h.	- 2			

Tableau III

Thermostabilité du cuir traité avec différents agents d'élimination des sels calcaires

Traitements	Cuir médiéval			Cuir du 19e siècle		
	contact	rinçage	ΔT °C	contact	rinçage	ΔT °C
Acide chlorhydrique 3 %	1 h.	6 h.	- 2	1 h.	6 h.	- 2
		20 h.	- 3		20 h.	+ 3
Acide phosphorique 3 %	1 h.	2 h.	- 10	1 h.	2 h.	- 10
		4 h.	- 2		4 h.	- 5
		6 h.	0		6 h.	- 10
		20 h.	0		20 h.	- 2
	5 h.	20 h.	0			
E D T A 5 % pH 10	1 h.	1 h.	- 10			
		6 h.	- 7			
		20 h.	- 8			
	3 h.	1 h.	- 11			
		6 h.	- 10			
		20 h.	- 8			

Tableau II

Thermostabilité du cuir traité avec différents agents complexants du fer

Traitements	Cuir médiéval			Cuir du 19e siècle		
	contact	rinçage	ΔT °C	contact	rinçage	ΔT °C
EDTA 5 % (pH = 4,5)	1 h.	1 h.	- 7	1 h.		
		4 h.	- 3		4 h.	- 10
		6 h.	0		6 h.	0
	3 h.	1 h.	- 9			
		6 h.	- 8			
		20 h.	- 4			
	4 h.	20 h.	- 6			
	12 h.	6 h.	- 8			
		24 h.	- 8			
Hexamétaphosphate de sodium 5 %	1 h.	1 h.	- 10	1 h.		
		2 h.	0		2 h.	0
		4 h.	0		4 h.	0
	3 h.	1 h.	- 10			
		6 h.	- 7			
		20 h.	- 3			
Coriagen K 1 %	1 h.	6 h.	+ 2	1 h.	6 h.	- 7
		24 h.	0		24 h.	0
	3 h.	1 h.	- 10			
Coriagen K 2 % (pH = 3)	1 h.	6 h.	- 6	1 h.	6 h.	- 4
		24 h.	0		24 h.	0
	3 h.	1 h.	- 10			
		6 h.	- 7			
		20 h.	- 5			
Citrate d'ammonium 5 % (pH = 5,3)	2 h.	6 h.	- 0	2 h.	6 h.	0
	3 h.	1 h.	- 10			
		6 h.	- 6			
		20 h.	0			
Acide citrique 3 %	1 h.	2 h.	- 4	1 h.	2 h.	- 8
		20 h.	+ 2		20 h.	+ 3
Acide citrique 5 % (pH = 1,5)	1 h.	4 h.	+ 3	1 h.	4 h.	- 2
		6 h.	+ 3		6 h.	- 2
	3 h.	1 h.	- 5			
		4 h.	+ 2			
		6 h.	0			
Acide oxalique 5 % (pH = 1,5)	½ h.	1 h.	- 20	½ h.		
		4 h.	- 6		4 h.	- 8
		6 h.	- 6		6 h.	- 8
		20 h.	- 3		20 h.	+ 3
	3 h.	1 h.	- 7			
		6 h.	- 7			
		20 h.	- 6			

MMARY

ricultrual scientists have een exploring containment CO_2 as a potentially safe thod of fumigation; but ere have been no published sts up to now on the fects of CO_2 on museum ob- cts.
is experiment tests the sk of pH changes in orga- c materials. Containment CO_2 for three days had no fect on the pH of the four terials tested.

EFFECTS OF CO_2 FUMIGATION ON pH

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1071 EA Amsterdam, The Netherlands

Introduction

It is difficult to get museum objects fumigated by methods that are safe for both the objects and the people who will be handling them. Sending objects to a fumigator specializing in museum objects does not necessarily insure proper treatment, as was discovered when "expert" fumigators in the New York City area offered only two options for fumigating a buffalo hide infested with odd beetles. One, methyl bromide fumigation, could have greatly weakened the hide because of bromine replacing sulfur in the protein molecules. The second option, ethylene oxide, has the disadvantage of settling in fatty materials of leather, retaining thus a residual toxic effect toward humans as well as insects. This can be ameliorated by thoroughly airing the fumigated objects for several weeks (1); however, the fumigator was unwilling to keep the hide in question for more than two days.

Clearly, other options must be explored. The United States Agriculture Department has been investigating the use of controlled atmosphere storage for insect control since 1965 (2). CO_2 concentrations as low as 60% have been shown to kill most species and life stages of stored-product insect when maintained for four days (3).

This method could be especially good for museums, as it is safe enough for use by untrained persons, and it requires little more than an airtight container or vacuum tank, and a pressurized cylindar of CO_2. Unlike most fumigants, CO_2 is a normal part of the air, and any escaping gas will be immediately diluted to a safe concentration.

However, no work has been published up to now, on the effect of containment in a CO_2 atmosphere on the materials contained. One potential problem is the risk of CO_2 reacting with free water in the atmosphere or in the fumigated materials, to form carbonic acid. This paper tests that risk.

Experimental design

Four organic materials that might be encountered in museum objects, either fine art or ethnographic, were chosen for testing: dyed 70% rag paper (Canson Mi-Tientes in bisque), 100% wood pulp paper (cheap cardboard), eucalyptus bark, and vegetable tanned goat skin. Small samples, approx. 0.5 x 1.0 cm, were cut from each. The pH of each was measured using Merck special indicator papers scaled at intervals of .2 to .3 pH units. The papers were pressed for one minute with a glass plate, onto a small drop of distilled water on the surface of the sample.
One sample of each type was placed in the experiment chamber (see fig. 1). CO_2 was supplied from a pressurized cylinder. The relative humidity was kept at 63 + 8% by passing the gas through a wash bottle containing 87% glycerine and 13% water, before releasing it into the chamber. This somewhat high humidity was kept both to insure the availability of free water for possible reaction with the CO_2, and to reflect a real necessity in fumigating sensitive objects that might need to be kept at a constant r.h. to prevent warping or cracking.*

The CO_2 was fed in from the bottom of the chamber. Because CO_2 is heavier than oxygen or nitrogen, the air inside the chamber was pushed out through the exit tube at the top of the chamber, which was sealed off with a stop-cock after sufficient CO_2 was run through.

After 72 hours the samples were removed, and the pH of each immediately remeasured. Three more trials were run by the same methods.

* In practice, it may be preferable to maintain a constant r.h. with saturated salt solutions kept inside the fumigation chamber, instead of with a wash bottle. The insects being killed may take in water in response to high CO_2 concentrations (4), thus modifying the ambient r.h.

Results

In all four trials, there were no pH changes significant enough t be measured with the pH strips (see table).

Conclusion

CO_2 fumigation appears from this test to be a safe method fo museum objects, as well for museum personnel. More research shoul be done, however, on potential pH changes in other materials ar on effectiveness against the specific insects that plague museums

Acknowledgements

To Andreas Georgiades and Andreas Papadopoulous of the Cypru Museum, Conservation Laboratory, and Thomas Varellias of th Cyprus Ministry of Agriculture, for their assistance in obtainin equipment and materials for this experiment; and to Dr. Rober Davis, Director of the USDA Stored Product Insects Research an Development Laboratory, for supplying me with all the infromatio the USDA had available on CO_2 fumigation.

Notes

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3. Jay, Edward G.; "Suggested conditions and procedures for usin CO_2 to control insects in grain storage facilities" USDA Agricul- tural Research Service Miscellaneous Publication no. 51-46

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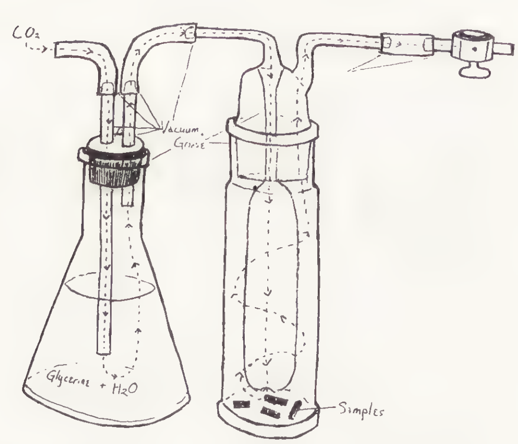

Fig. 1

	Trial 1	Trail 2	Trail 3	Trail 4
Hide before	5.1	5.4	5.4	5.1
after	5.1	5.4	5.4	5.1
Bark before	6.1	6.4	5.8	5.8
after	6.1	6.4	5.8	5.8
Card before	5.1	5.4	5.1	5.1
board after	5.1	5.4	5.1	5.1
Canson before	5.1	5.4	5.4	5.4
paper after	5.1	5.4	5.4	5.4

table 1

Working Group 19

Easel Paintings on Rigid Support

Peintures de chevalet sur supports rigides

EMBERS

.T. Davila Alvarez - Spain
. Davila Alvarez - Spain
. Bjarnhof - Denmark
. Brough - England
. Bergeon - France
. Dies du Rojas - Mexico
. Cortet - France
. d.C. Garraido P - Spain
. Hanssen-Bauer - Norway
. Hemmet - England
. Kaland - Norway
. de Keijzer - Holland
. Krist - Austria
. Lautratte - France
. Leegenhock - France
. Lewis - England
. Lokma - Egypt
. van de Maele - Belgium
. MacNaughtan - Australia
. Maresh - Fed. Rep. Germany
. Odekirk - U.S.A.
. PembertonPigott - England
. Pfister - Switzerland
. Sandner - GDR
. Ramsay-Jolicoeur - Canada
. van Schoute - Belgium
. Seidl - Austria
. Timm - GDR
. Vērougstrate - Belgium
. Viana - Portugal

TRIENNIAL OVERVIEW

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Not much has been published on the technology and conservation techniques of easel paintings on rigid supports, such as copper, tin, iron, or on the making of reverse paintings on glass. For a time, panel paintings got some special attention in terms of dealing with conservation problems of the wooden support, but lately few research projects are known. Practically no literature exists about painting on slate, marble or semiprecious stone, like lapis lazuli for example. No relevant bibliographies have been published, besides a recent paper on copperpaintings in England (Isabel Horowitz in Conservator, no. 10, 1986 UKIC).

Because of this situation we formed the working group during the latest Triennial Meeting in Copenhagen. No major activites with regard to the whole membership of the working group took place, but the coordinator could call the attention to this neglected field during the 'Specialist Review State of the Art in Paintings Conservation' at the Getty Conservation Institute and make it accepted as one of the priorities to be taken care of. I therefore hope to be able to organise some special meeting of this group during the period after Sydney.

The AIMS of our work are:

To collect and publish
- information on technologies, making techniques and production processes
- treatment reports
- information about old and new treatments and and methods, successful one as well as failing ones
- data on care and handling.

To instigate
- research into technology, material engineering problems, treatment...
- assembling of bibliographies on the history, technology and conservation of particular types of rigid support paintings.

To define
- typical conservation problems of specific types of supports and rigid support paintings
- specifically dangerous conservation treatments related to particular phenomena like interaction of solvent and metal
- the particular taken and the precautions to be taken in handling, framing and packing.

Some of these topics are already addressed in this year's preprints' contributions, others were promised, but circumstances did not allow for their realisation; others will be published later.

To date the working group consists of about 30 members from eighteen countries and there will be more: join!

MMARY

e article describes treatment of
intings on copper supports, es-
cially flaking provoked by cor-
sive compounds. Benzotriazole
discussed as an inhibitor for
pper corrosion. Various consol-
ants are examined. Synthetic
ues with a neutral pH, e.g. Pa-
loid B 72 and Incralac, are gen-
ally recommended.

TREATMENT OF PAINTINGS ON COPPER SUPPORTS. SOME EXPERIMENTS AND OBSERVATIONS

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Introduction

The Royal Museum of Fine Arts in Copenhagen has a number of paintings on copper supports. A renewal of interest in conservation problems, especially flaking, arose when the conservation department received for conservation eight paintings on copper support showing various degrees of flaking.

These paintings were well known to us, having been examined and treated several times throughout the years. The effect of all previous fixations of flakings, however, did not last long.

Very little has been published about the subject (Dr. J.A. van der Graaf[1)] and I. Horowitz[2] e.g.), and even less has been written about treatments. With this background a more practical approach to the problem was needed, and information on treatments by Danish conservators of paintings on copper supports in the last 6-7 years was collected.

Discussion

It seems that the most frequent damages were flaking and cleavages provoked by a corrosive compound found between the copper plate and the painting structure directly visible and also obvious in cross-sections. The flaking includes varnish, paint, and ground down to the copper plate. Together with conservators and chemists from The National Museum and The School of Conservation we discussed possibilities for conservation treatments[3]. It was agreed that corrosive compounds in the form of crystals could not be reduced by chemical means but could only be mechanically removed and only in places where the paints had already flaked off.

The next question was whether corrosion can be prevented or stopped. It was of interest to discuss the good results obtained by treating archaeological bronzes and copper alloys with benzotriazole, BTA ($C_6H_5N_3$) as an inhibitor[4,5]. According to Helge Brinck Madsen, who has been treating archaeological bronzes with BTA for 2o years, this is an effective remedy against corrosion. In 1984 he examined more than 6oo objects previously treated with BTA, and found only a few showing traces of corrosion not completely stopped.

When BTA is in contact with copper, it is considered to form a thin, chemically bonded complex, cuprous benzotriazole, on the surface, where it reinforces the protection already afforded by the naturally occurring oxide film. The copper-benzotriazole molecule is thought to be produced by the substitution of a cuprous ion for a hydrogen ion in the nitrogen-hydrogen group[6].

To achieve a good result of this treatment it is important to clean the metallic surface of the object. But in the case of a copper plate covered with a layer of paint it is not possible to clean the metallic surface under the painting. However, the application of BTA will stop or at least inhibit corrosion, when BTA is penetrating in cracks and porosities. Different ways of applications were proposed:

1) A bowl of BTA powder placed together with the painting in a closed box. After some time vapours of BTA should affect the copper plate. This method was rather slow, and verification of the result was difficult - even by microscope.

2) A quicker method was to dissolve BTA in ethanol or water and apply this solution to the painting. However, fearing possible reactions, risks were not taken by applying the solution directly to the paint, but only to areas of lacunae, using a 3% by weight solution.

3) BTA could also be added to the consolidant used for fixation of flaking paint. E.g. Incralac (= Paraloid B 44 with BTA. Furthermore an absorber for ultra-violet light has been added). The same result could be obtained by adding 1% BTA dissolved in ethanol to Paraloid B 72. In any case, the consolidant must be neutral (pH 5-6) like e.g. Paraloid B 72, Incralac, and Plexisol 55o P.

Still one problem has to be examined: the possible effect of BTA on copper-compound pigments, e.g. azurite.

Practical experiences

The choice of consolidant was discussed on the basis of practical experience from conservation treatments carried out in Denmark in recent years. Neither linseed oil and waxes, nor organic glues have proved to be satisfactory. The

most convincing group of consolidants appears to be Paraloid, Incralac, and Plexisol 55o P. Below are excerpts from some unpublished records of restorations dealing with stabilization of layers of paint on copper supports.

1) Attributed to Domenico Zampieri: The Coronation of the Virgin. About 163 K.M.S. Sp.no. 1o9. 32,8 x 31,6 cm. Report by Winnie Odder, The School of Conservation, 198o[7].

Various consolidants were tried - among others sturgeon glue (5-1o% solution). The adherence proved to be too weak. Finally Paraloid B 72 (1o% solution) was applied with a satisfying result.

2) Unknown Dutch/German Master: Aurora. About 1625. Rosenborg Castle. 43,3 x 29,5 cm. Report by Boel Biel, The School of Conservation, 1984[8].

Experiments were made with various consolidants. Finally, polyvinylacetate, medium-viscous, in toluene (1o% solution) was chosen. The polyvinylacetate solution was applied on flaking areas, and after 3o-6o minutes the paint was treated with a heated spatula (5o° C). The result proved to be satisfactory. Treatment with BTA was abandoned considering the incertitude of the effect of direct contact of BTA with cuprous pigments, e.g. azurite.

3) Attributed to Henrik Ditmar: Family Portrait, Anders Schultz. 1652. (Epitaf with painting on copper plate). Holbæk Museum. 64 x 98 cm (oval). Report by Stephanie Noerbel, The National Museum, 1981.

14 consolidants were tested directly on copper to control possible discoloration of the metallic surface. Eight of these in varying degrees had a negative effect on the metallic plate:

sturgeon glue
skin rabbit glue
bees' wax
microcrystalline wax
Acronal 3oo D
Plextol D 36o
Plextol D 36o + o,5% BTA

- whereas 6 had no traceable effect on the metallic surface:

Plexisol 55o P in toluene
Paraloid B 72 in xylene
Paraloid B 72 + o,5% BTA
Paraloid B 44 in toluene + 1,5% BTA
Ketone resin N in white spirit
dammar in turpentine

Out of these Plexisol 55o P was chosen as a consolidant for the painting in question.

4) Unknown Master: Portrait of Constant Sennepart (1625-17o3). Bibliothèque Wallone, Amsterdam. 11,o x 9,o cm (oval). Report by Beate Federspiel. Centr Laboratory, Amsterdam.

"The paint layer is fixed with Plexisol P 55o dissolved in toluene 1:2. The cuppings are layed down by a slight pressure before the complete drying of the Plexisol".

5) Abraham Wuchters: Portrait of a Noble Boy in Cupid's Costume. About 165o K.M.S. Inv.no. 3727. 82 x 64 cm. Report by Helena Berlowicz, The Royal Museum of Fine Arts, 1981.

Generally, the condition of the painting was good with proper adhering of the paint to the copper support, but damaged by mechanical scratches. Corrosive compounds were formed around these damages. After the painting was cleaned, it was not possible to remove the corrosion product mechanically. Paraloid B 72 was used as a medium for inpainting. Furthermore, it was applied in a layer for insulation against air and humidity, serving also as a final varnish.

Dark spots could be observed under the semi-transparent carnation of Cupid. These spots seem to be sporadic oxidation of the copper support under the layer of paint.

6) Willem von Herp: Landscape with Atalante's Hunting. About 164o. K.M.S. Inv.no. 72o9. 4o,5 x 53,5 cm. Report by Mette Bjarnhof, The Royal Museum of Fine Arts, 1983.

The whole surface of the painting was characterized by small flakings and considerable mechanical damages.

The flakings were consolidated with Paraloid B 72 (2% in xylole) and slightly pressed down with a cold spatula.

The varnish was removed, and after retouching replaced with one layer of Paraloid B 72, followed by a sprayed application of Ketone resin N as a finishing coating.

7) Frans van Mieris the elder: Portrait of a Painter. About 1675.
K.M.S. Sp.no. 562. 22,5 x 16,5 cm.

Frans van Mieris the elder: Portrait of a Lady. About 1675.
K.M.S. Sp.no. 563. 22,5 x 16,5 cm.

Reports by Mette Bjarnhof, The Royal Museum of Fine Arts, 1986.

The two portraits have been in the collection since 1763, both presently showing heavy general flakings. During the past the paintings have been treated several times, e.g. recorded in 1908, 1909, 1913 and 1939. The report from 1909 even mentions earlier treatments by restorer Andersen, working with the collection from 1887-1906.

By tradition the paintings have been treated according to Max von Pettenkofer's method [9] The Royal Museum catalogue (1951) mentions, "In 1904 the picture was almost completely spoiled by the Pettenkofer process".

For several years the paintings have been flaking to such an extent that they must remain in a horizontal position to prevent loss of paint.

Former records mention gelatine as a consolidant, and an examination shows that bees' wax also has been used. Obviously, the general flaking was the result of the formation of a crystallic corrosion between the copper supports and the layer of paint - visible with the naked eye and in cross-sections.

Frans van Mieris the elder: Portrait of a Painter. After restoration.

The Portrait of a Painter was first selected for treatment.

The above mentioned discussion and recommendation resulted in the application of Incralac (Paraloid B 44 + BTA) as an attempt to stop the vigorous development of corrosion and as a first fixation of flakings. This treatment was repeated several times, after which the surface was evened out with a cold spatula.

The exposed metallic surface in all lacunae was treated with a 3% BTA solution in ethanol.

The varnish has lost its transparency due to a fine pattern of cracks. The unfortunate Pettenkofer treatment mentioned previously seems to have affected the dark and black coloured areas of the portrait. Thus, there was no well defined boundary between the paint and the varnish. Consequently, no attempt was made to remove the varnish, however, to regain better transparency a mixture of solvents was lightly sprayed on the painting[10].

After the inpainting of lacunae, a final varnish of Ketone resin N was applied [11, 12].

The conservation process of the Portrait of a Painter will be evaluated before treatment of the pendant, Portrait of a Lady.

Frans van Mieris the elder: Portrait of a Lady. Before restoration.

Conclusion

Although BTA has proven its efficiency within the field of archaeology this inhibitor has had no immediately observable effect in relation to corrosion on paintings on copper supports. The treated paintings, however, are under constant observation.

Nevertheless, it might be necessary to examine the risks for any chemical reaction between BTA and copper compound pigments.

In all seven reports presented, organic glues, e.g. gelatine, sturgeon glue and such dispersions as Plextol, PVA, have been rejected, and consolidants as Paraloid B 72 and Incralac have in most cases been preferred. An overall impression is that Paraloid B 72 with BTA added matches Incralac as a consolidant. Both are good adhesives and do not demand any heat during the fixation process. Likewise, both Incralac and Paraloid B 72 with BTA added are compatible with Ketone resin N, and can be used as a finishing varnish.

The following persons have taken part in discussions concerning the item:

3) The School of Conservation:

H. Brinck Madsen, Conservator
B. Federspiel, Conservator
M. Christensen, Chemist
V. Hjelm-Hansen, Chemist

The National Museum:

S. Noerbel, Conservator

The Royal Museum of Fine Arts:

H. Bjerre, Conservator
E. Berlowicz, Conservator
L. Bøgh, Conservator
J. Glob, Conservator
M. Bjarnhof, Conservator

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Studies in Conservation, vol. 16, 1971, pp. 12o-122.

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Published by The United Kingdom Institute for Conservation.

7) Winnie Odder: Klimaskadet maleri fra Badstuehuset.
Afgangsopgave på Konservatorskolen, 198o. Det Kgl. Danske Kunstakademi, Konservatorskolen.

8) Boel Biel: Maleri på kobber.
Afgangsopgave på Konservatorskolen, 1984. Det Kgl. Danske Kunstakademi, Konservatorskolen.

9) Max von Pettenkofer: Über Ölfarbe und Conservierung der Gemälde-Gallerien durch das Regenerations-Verfahren.
Braunschweig, 187o. Verlag von Friedrich Vieweg und Sohn.

1o) R.L. Feller, E.A. Jones, N. Stolow: On picture varnishes and their solvents. (Reforming: 4 parts of ethylalcohol, 1 part of diacetonealcohol, 1 part of cellosolve acetate).
Intermuseum Conservation Association. Oberlin, Ohio, 1959.

11) E. de Witte, M. Goessens-Landrie, E.J. Goethals, K. Van Lerberghe and Van Springel: Synthesis of an acrylic varnish with high refractive index.
ICOM. 81-16-4.

12) E. de Witte, M. Goessens-Landrie, E.J. Goethals, R. Simonds: The structure of "old and new" Paraloid B 72.

Materials:

Incralac (The British Domolac Co. Ltd., Abbey Wood, London, S.E.2).
(Transformation points, Tg, 6o° - Hardness, Tukan, 15-16).

Paraloid B 72 (Rohm und Haas)
(Transformation points, Tg, 4o° - Hardness, Tukan, 1o-11).

Plexisol and Plextol (Röhm).

Polyvinylacetate (B.D.H.).

HINTERGLASMALEREI/REVERSE PAINTING ON GLASS IN 18TH AND 19TH CENTURY SOUTHERN GERMANY - RECONSTRUCTION OF 6 "HINTERGLAS" TECHNIQUES

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SUMMARY

The object of this paper is to present a brief description of the history, composition and some reconstruction methods of "Hinterglasmalerei" from Southern Germany in the 18th and 19th centuries. The "Hinterglasmalerei" is a type of painting which is painted on glass. In order to be able to create methods for the conservation and restoration of such paintings it is important to understand the relations between glass, binders, layers of paint and the functioning of various, and different, techniques used. 6 of the most typical "Hinterglas" techniques mentioned in the relevant literature were chosen for reconstruction.

The paper does not pretend to be exhaustive, but is meant as a source of inspiration for further studies of the paintings and of the possibilities for their conservation and restoration.

INTRODUCTION

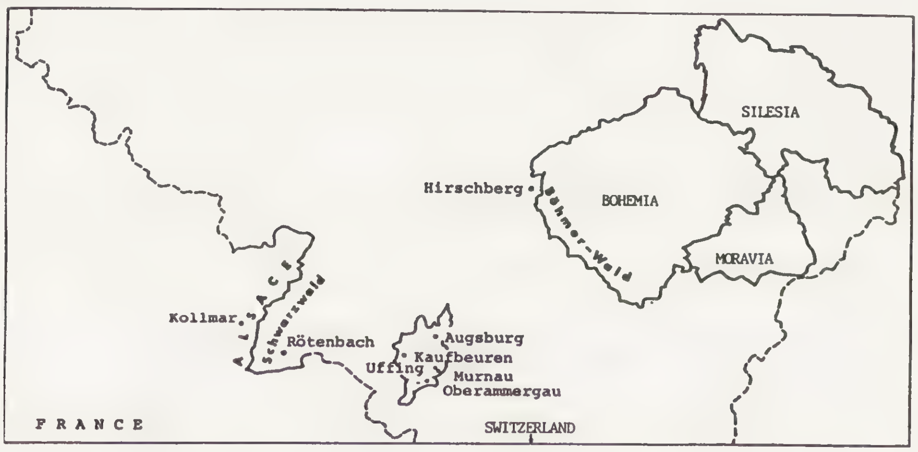

Fig.1. Map of "Hinterglas"-producing towns and regions in Southern Germany.

"Hinterglasmalerei", or reverse painting on glass, is a technique conveniently grouped with similar glass techniques, such as stained glass, enamel glass, etc.. However, unlike such techniques, which apply colour by means of a melting process, the "Hinterglastechnique"adds colour directly to the reverse side of a sheet of glass; it goes back to 13th century Italy and was originally intended to be an imitation of enamel glass, or was used as ornamentation on furniture and the like. The use of "Hinterglasmalerei" in the shape of individual, independent paintings is a baroque phenomenon especially popular in Southern Germany and part of todays Czechoslovakia (see fig.1), most often in the form of copies of engravings or oil-paintings. Later on the interest for such paintings increased among all kinds of people, so a mass-production of most "Hinterglasmalerei"'s set in, which deprived the pictures of individuality. Towards the middle of the 19th century "Hinterglasmalerei" was ousted by the introduction of colour lithography. Since then the technique has seen only sporadic revival, for instance through the works of some German expressionists.

In the actual painting process the paint is applied directly to the reverse side of the glass, which thus functions both as the supporting base of the painting and as the protecting surface varnish. As the painting is intended to be viewed from the front, but is actually painted from the back, the entire painting process must be reversed, and the various layers of paint must be applied in an order opposite to the one of conventional painting.

The painting, then, is painted in reverse: details and highlights are applied first, then larger areas of paint, and finally the background; thus correction of errors made while painting, is made virtually impossible. Before the work is begun a "Riss" (1) may be made, that is a reverse line drawing of the contours of the original. The "Riss" is placed under the sheet of glass and serves as an indispensable guide during the painting process.

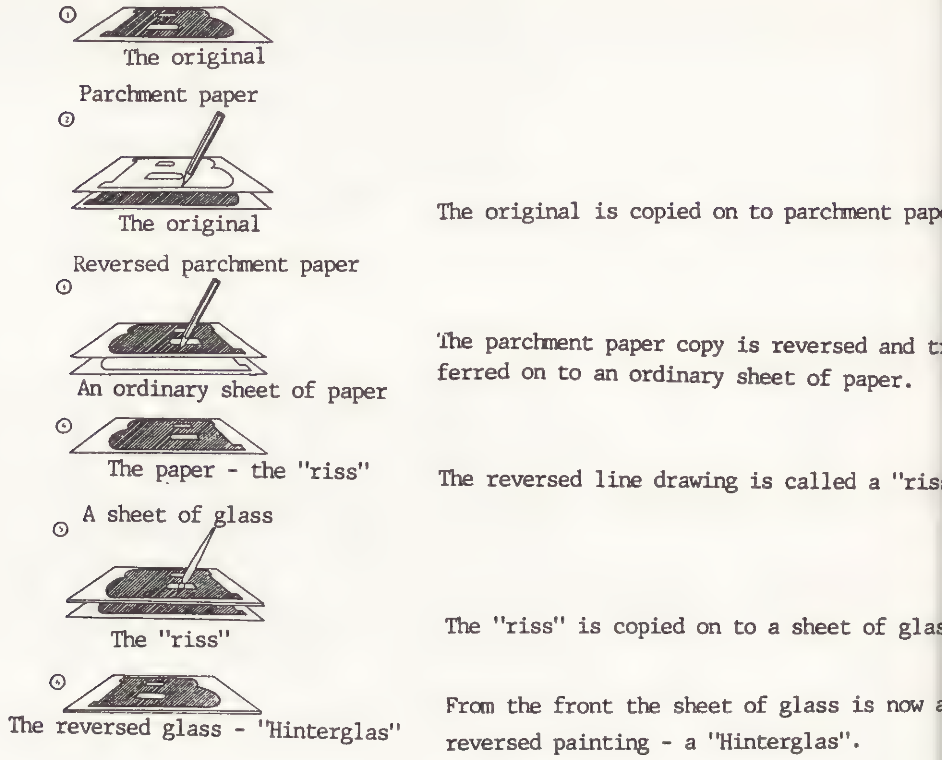

Fig.2. Normal working method for the production of a "Hinterglasmalerei".

RECONSTRUCTION

For the reconstruction six "Hinterglas" techniques were chosen, of which three were "full-size" reconstructions, that is the production of an entire painting to check the technique and its effects in all aspects (A); three others were "partial", comprising only a section of the original to illustrate particular effects of the technique (B). The techniques were the following:

1) A "Cartouche" picture (A)
2) Two "Goldradierung"s (A)
3) A "Spiegelschliffmalerei" (B)
4) A "Spiegelmalerei" (B)
5) A "Goldschliffmalerei" (B)
6) A "Rauchbild" (A)

DESCRIPTIONS OF METHODS

For the reconstruction of the techniques dealt with, ordinary 2mm window glass was used, cut into pieces of 18 by 14 cm (A), and 9 by 14 cm (B). Before the re construction began, the glass pieces were carefully washed in soap and water and then wiped with ox gall to remove surface tension and any remaining grease, in this way ensuring that the paint would adhere to the glass in the best possible way. To guide the painting process "Risses" were made of the originals.

MATERIALS USED

Binders: Glair (2) for the laying of gold.
12-hour gilding oil.
Caseine dissolved in ammonia and water.
Linseed oil.
Gum Arabic.
Laquer.

Pigments: Burnt Cyprian Umber, Charcoal black, Chrome Yellow, Golden Ochre, Indigo, Madder Lake, Prussian Blue, Raw Umber, Vermillion, Viridian, White Lead

Other materials: Ox gall, gold leaves Windsor & Newton Black Indian Ink and a glass engraving tool.

RECONSTRUCTION NO.1 A "Cartouche" picture

Fig.3 "Riss" for "H. Herz Maria". Cartouche picture from Oberammergau, ab.1850
(Original 20 by 13 cm.) (3)

The first picture used for reconstruction was a cartouche picture from Oberammergau in Southern Germany (see fig.1). Much folk art was produced there since the 16th century, but "Hinterglasmalerei" was not conspicuous until the mass-production period after the middle of the 18th century. At that point several workshops began simplifying and stylizing the pictures in order to speed up the work process; this is the origin of the so-called "Hinterglas-Typusbilder". Such paintings often present saints or biblical characters set in a so-called cartouche, that is a kind of square or circular frame.
"H. Herz Maria" (see fig.3) is a painting typical of this region, and the technique that confines itself exclusively to applying paint to the reverse side of the glass is by far the most common of the "Hinterglas" techniques.
Before the actual reconstruction began, test sheets of glass were prepared to establish which binder would be the best, and to decide on the order of the layers of paint. The relevant literature (4) recommended Gum Arabic, caseine, and oil as binders.
Gum Arabic proved inapplicable as it did not adhere to the glass but peeled off. Therefore caseine, which could best be finely applied, was used for contours and details, while larger areas of paint were laid in oil. The procedure for the execution of the painting is as follows:

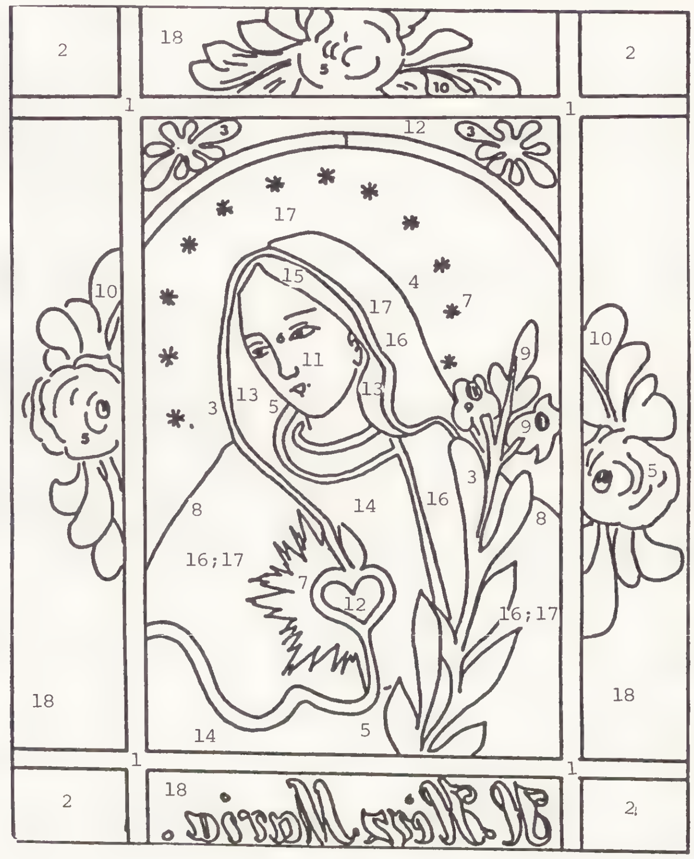

Fig.4

1. The "Riss" (see fig.3) is placed under the glass, and the dark cartouche lines are transferred to the glass in Charcoal Black in caseine.
2. The corners of the cartouche are gilded with glair.
3. Gold leaf is laid in gilding oil in the contours of the cloak and in the flower.
4. The contours of her face are painted in Burnt Cyprian Umber in caseine.
5. Shades in the robe, about her mouth, and in the flowers of the cartouche a painted in Madder Lake in caseine.
6. The eyes and the letters of the legend are applied in Charcoal Black in ca- seine.
7. The stars above Maria are laid in White Lead.
8. The shades of the cloak are painted in Indigo in caseine.
9. The flowers in front of Maria are painted in White Lead in linseed oil.
10. The leaves of the flowers in the cartouche are now made with a mixture of Chrome Yellow and Viridian in linseed oil.
11. White Lead and Golden Ochre are now mixed for the carnation, under which i applied a faint tinge of Madder Lake for the cheeks.
12. The heart and the arch above Maria are painted in Vermillion in oil.
13. The lining of Maria's cloak is painted in Chrome Yellow in linseed oil.
14. A transparent layer of Madder Lake is applied to her robe.
15. Her hair is covered with Umber.
16. The cloak is filled in in Prussian Blue in oil.
17. The entire mid-area is covered with a mixture of Prussian Blue and White Lead in oil.
18. The last colour to be applied is White Lead in oil in the squares of the cartouche.

The building-up of the pictures might change slightly from one workshop to an- other. In our reconstruction we combined what was to be seen in the Colour Pla (5) with what the test sheets indicated, and with what could be found in the re levant literature (6).

The result may be seen in these photos:

Fig.5 a and 5 b.

RECONSTRUCTION NO. 2. Two "Goldradierung"s.

Fig.6. Photo of the original "Goldradierung": "Das Ende Eines Kapitalen"
Joseph Anderle, West Bohemia, 19th century (Original 33 by 25 cm.) (7)

The next picture is a so-called "Goldradierung" from Bohemia (see fig.1). The Bohemian "Hinterglas" techniques go back very far; techniques like them are described in antiquity and mentioned, for instance, by Cennino Cennini in the 15th century. It is characteristic of them that they avail themselves of the techniques of the glass industry rather than those of the painting tradition. Direct processing of glass - by hatching, cutting, or coating, for instance with metal - came to be predominant in this region.

Such techniques were kept alive over the years, from purely ornamental decoration to expressive, individual paintings, but they were not exposed to the simplification and stylization of mass production.
A "Goldradierung" is achieved when lines are hatched or areas erased in a layer that covers the back of the glass and a contrasting material is later applied. This means that if the hatching is made in a black layer, gold is applied to make the contours and areas erased stand out in contrast; conversely a hatching in a layer of gold can be given contrast by the application of a layer of black. Such contrasts will usually have a highly graphic effect.

"Das Ende Eines Kapitalen" is an exquisite example of this type. It is a fact (8) that a "Radierung" like this one can be made in two different techniques; to examine and at the same time illustrate them, both were employed in the reconstruction.

Some tests were made to ascertain which binder was to be used for the gold in order to create the best foundation for hatching, simultaneously ensuring a firm adhesion of the black pigment to the glass. It was decided to apply the gold in oil, since it facilitated the hatching, and the burrs would be sufficiently broad to let the black colour stand out in clear contrast.

Once again Gum Arabic was rejected, whereas ordinary ink covered well and was ideal for hatching.

Subsequently two "Goldradierung"s were made:

1. Hatching in gold:

The glass is covered with gilding oil and is left to dry for about 12 hours. Then the entire reverse side of the glass is covered in gold. A "Riss" cannot be used in these cases as it does not show through the gold and the black. It is possible, however, cautiously to mark off the main contours in the gold wit[h] a soft pencil. Then the hatching is made. The picture is modelled and formed by varying the density of the hatching and erasing of the areas; the process i[s] very similar to the ordinary graphic engraving on metal sheets.

When the hatching is finished a covering layer of black is applied. It must be so thick that it completely fills in the hatchings, at the same time protectin[g] the vulnerable burrs. When viewed from the front the picture now clearly presents the hatched areas and lines in black contrast to the gold (9).

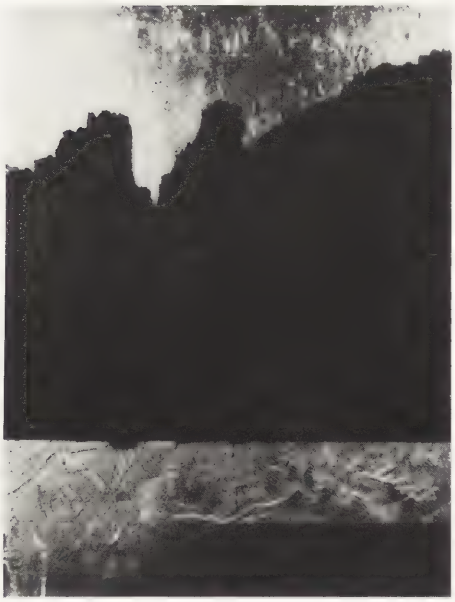

Fig.7 a and Fig.7 b.

2. Hatching in black:

A glass sheet is covered with ink, and when this is dry the hatching may begin. The main contours of the original are cautiously transferred to the ink. The in[k] must cover the entire back of the sheet, but must not be too thickly applied as this will cause "splintering" in the black layer when the hatching starts. To achieve light areas the hatching will have to be dense to make the gold shine through properly. Dark areas require hatchings that are less dense. The picture

will be formed and modelled out of the dark background.

When the hatching is finished the entire back is covered with gilding oil. This is left to dry for 12 hours, and gold leaves are then laid on to the hatchings. With a soft brush the gold is firmly brushed into the oil, and when viewed from the front the hatched lines and erased areas will stand out in golden contrast to the dark piece of glass.

Descriptions of the hatching in black technique have not been found in relevant literature, so it has been constructed in an order opposite to the gold hatching technique described by Cennini.

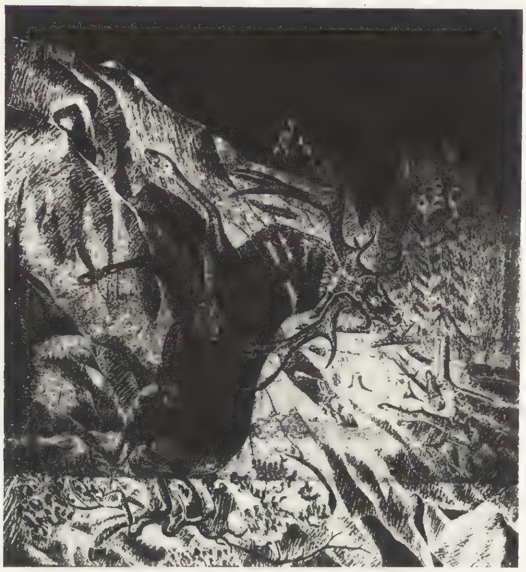

Fig.8. Photo of the finished "Goldradierungsbild".

In actual fact the two techniques are quite similar to each other, and "Goldradierung"s can be produced both ways with only slight visible difference.

The next three reconstructions have been made on a part of the same original. The intention was to illustrate the techniques rather than create finished paintings. Like the "Goldradierung" the three techniques are typically Bohemian:1. "Spiegelschliff", 2."Spiegelmalerei" and 3."Goldschliff". The original is "Hl.Florian".

RECONSTRUCTION NO.3 A "Spiegelschliff" picture.

Fig.9 Photo of the original "Spiegelmalerei": "Hl.Florian". Buchers, Bohemia. Beginning of the 19th century (Original 27 by 18,1 cm.) (10)

The metal coating and glass engraving techniques are typical of Bohemia, where also the first experiments with amalgam coating took place in the 18th century. The first step was the "Spiegelschliff" frames, which were decorated with finely engraved pieces of glass amalgamated with tin and mercury. Out of this technique grew the "Spiegelschliff" pictures which were made the same way as the frames but where the amalgamated glass now functioned as the picture surface itself. The engraved areas look light, almost white, on the amalgam background (11).

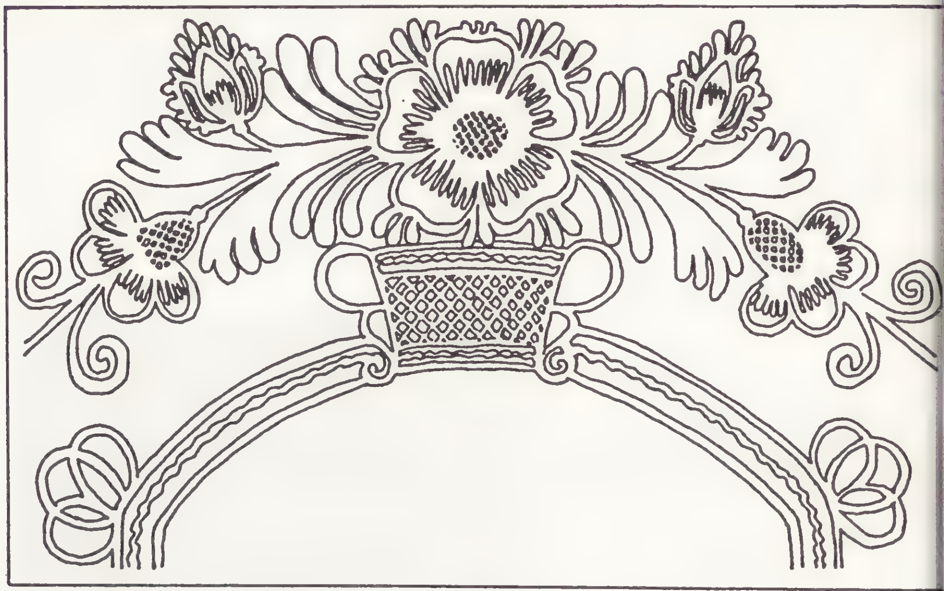

Fig.10. "Riss" for the decoration in "Hl.Florian" (see fig.9)

With a glass engraving tool we engraved the glass after it had been placed ove the "Riss" (see fig.10). After the engraving process, an amalgam coating - in this case an alloy of tin and mercury - was applied as follows:

1. A piece of tinfoil is smoothed out on a slab of marble.
2. Mercury is added, evenly spread over the tinfoil. Dust, etc., is removed.
3. A glass sheet is pushed across the tinfoil, the surplus mercury at the same time being squeezed out between the glass and the marble.
4. The glass is weighed down with cloth-wrapped weights and kept in press for 24 hours.
5. The glass is now turned over, and as one edge is slowly lifted upwards unti it is almost vertical, the surplus mercury runs off.

This process may take from just one week up to a whole month. During the pressing process the glass broke, but only in one place, so the reconstruction was almost successful.

Fig.11. Photo of the finished amalgam-coated "Spiegelschliff" (a), and "Spiege malerei"(b).

RECONSTRUCTION NO.4 A "Spiegelmalerei".

"Spiegelmalerei" is a combination of painting and amalgam coating; such pictur are frequent in the late baroque an rococo periods (12).

They can be made in two ways:

1. The glass is painted on the reverse in the normal manner, and then the whol sheet is amalgamated. This is the oldest technique, but it gave way to an easier one:
2. Hatchings and erasures are made in a sheet already amalgam-coated, and pair is then applied. This method will leave rather blurred contours as the mercury does not cover the entire painted expanse, a fact that quickly reveals that this technique is at work!

The original "Spiegelmalerei" technique may be described as follows:

The glass is placed over the "Riss" (see fig.10), and the picture is painted. chose white for the leafage, black and red for the flowers. An amalgam coating was then laid on to the painting. The actual process followed the pattern de-

scribed above, and the result may be seen in the photo fig.13.

RECONSTRUCTION NO.5   A "Goldschliff" picture

The "Goldschliff" picture is closely related to the "Spiegelschliff" type as regards both technique, and time, and place; it is made with the same glass engraving method, but no amalgam is applied, gold being laid directly on to the engraved lines and areas, while black is applied for the general background. From the front an almost three-dimensional effect against the black background! The technique, which goes back to the end of the eighteenth century, is often used in combination with paint. (13)

The "Goldradierung" is made in the following manner:
Once again the glass is engraved over the "Riss" (see fig. 10) as described in Reconstruction no.3. The engraved lines and areas are filled with a 12-hour gilding oil, and gold leaf is then firmly brushed into the oil, loose bits of gold being removed at the same time. After this the back of the glass is painted in ink, and when viewed from the front the picture will show the engraved places standing out in golden relief on a black background.

Fig.14. Photo of the finished "Goldschliff" picture.

RECONSTRUCTION NO.6.   A "Rauchbild".

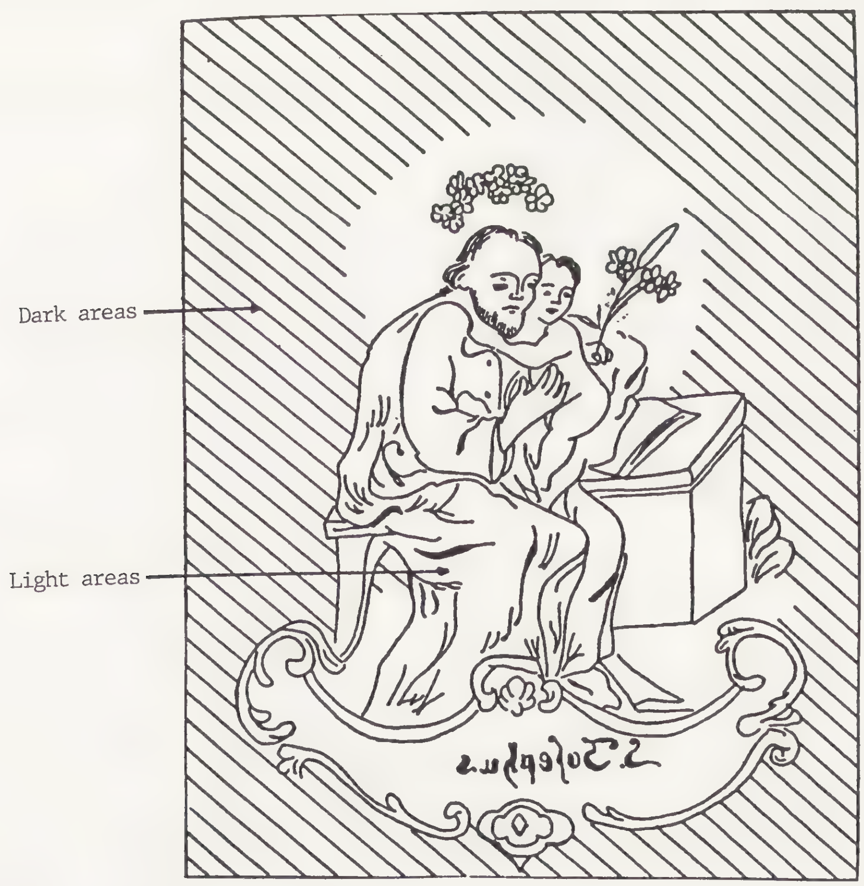

Fig. 13. "Riss" for the "Rauchbild": "St.Josephus", Seehausen, End of 19th century. (Original 34 by 27 cm.) (14)

The original for this reconstruction is a so- called "Rauchbild". It is the result of a rare technique from the second half of the 18th century. The pictures are meticulously executed and have delicate contours and light colours; they mostly present biblical scenes. In a "Rauchbild" a fine contour line drawing of the subject and ornamentation is made, and then the surrounding background areas are covered with soot from a candle, while the areas inside the contour lines are brushed clean. The layer of gold that is then applied to the entire back of the glass sheet, will then shine through only inside the contour lines. (15)

We made a few tests to make sure that the line drawing and the sooted areas

would bind to the glass when the glair for the gilding was added. It soon proved difficult to make the two materials adhere to the glass, so they had to be sealed off before the gilding was begun. The following procedure was used:

The "Riss" (see fig.13.) is placed under the glass, and the contour drawing is transferred in Charcoal Black in caseine. Where the background is meant to be completely black, black is laid in linseed oil. To protect and seal off the contour drawing a thin layer of linseed oil is applied over the entire back of the glass, and when this is dry the glass sheet is sooted by means of a candle.

Fig.14. The sooting of the glass already provided with contours and black area

When the glass has cooled off, a feather is used to brush the areas that are meant to appear light, and then gold leaf is laid in glair over the entire back of the glass sheet. From the front the gold now fills out the line drawings that are framed in black contours. Around them is a dark background of dark paint and soot. The brushing of the sooted areas may make the borderlines between gold and black almost indiscernible.

Fig.15. Photo of the finished "Rauchbild".

The six reconstructions described here do not exhaust the topic; nor do they represent the entire literature about it. However, actually performing such reconstructions will lead to a better understanding of the composition and the structure of "Hinterglasmalerei" and convey an idea of how the often forgotten "Hinterglas" pictures can be conserved and restored so that their layers of paint and gold will not be allowed to peel off their support.

NOTES

1) "Riss" is German for "sketch".
2) Glair is eggwhite whipped in water (1:1).
(D.V.Thompson: The Practise of Tempera Painting. p.55.)
3) Max Seidel. Colour Plate no.10. "H.Herz Maria".
4) Fride Wirtl.pp. 87 and 88.
5) Max Seidel. Colour Plate no.10. "H.Herz Maria".
6) Fride Wirtl. pp. 87 and 88.
7) Gislind Ritz. p 123. "Das Ende Eines Kapitalen".
8) Gislind Ritz. p. 159.
9) Cennino Cennini. chap. 172 pp. 112 to 114.
10) Gislind Ritz. Colour Plate no. 17. "Hl.Florian".
11) Wolfgang Brückner. p.83.
12) Wolfgang Brückner. p.83.
13) Wolfgang Brückner. p.84.
14) Fride Wirtl. p. 59. "St Josephus".
15) Fride Wirtl. p. 61.

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All illustrations have been made by the authors.

SUMMARY

This text sums up the results obteined putting a flemish painting of the 15th century, the triptych of Clenens VIIth, kept in the cathedral of Cagliari, under diagnostic analysis. These results will be useful for the painting restauration and also to establish the author of this very valuable work of art, just about unknown outside Sardinia. The reaserches are:
- Infra red photography
- Reflectography
- U.V.
- Radiography
- Microchimical, physical, quality of colours analysis.

They have been done by: E. DI. TECH. of Florence.

Pic.2 - Left table Reflectography I.R. Child

THE TRIPTYCH OF CLEMENS VIIth. DIAGNOSTIC ANALYSIS.

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In Sardinia exists an oil painting on wood in the treasure of Cagliari cathedral, just about unknown outside this region. It is certainly a flemish triptych but of controversial attribution and dating (pic.1 altogether view). This painting has been put through various tests with the aim of getting valuable information to complete the diagnostic scheme and therefore, to be more sure towards the imminent restauration.
The local authorities have never bothered with this work. The first one to talk about it , was the French poet Paul Valery, in his journey to Sardinia, that wrote in his diary "L'auteur est inconnu; mais on peut à la beautè de l'ouvrage, conjecturer raisonerablement qu'il est de peu anteriorieur à l'année 1527, époque ou florissait l'école de Raphael, disperséé par cette catastrophe. Il doit appartenir à l'un de ces grands artistes, et certes il ni y avait point de croutes dans la chambre à coucher du Médicis, cousin et second successeur de Léon X". (Note 1)
We can see that even if he was astonished by the beauty of this work, he put it in a cultural environment totally extraneous to it. In 1861 the canon G.Spano who studied archaeology and art, gives a different interpretation: "older than a century ..... some conoisseurs would attribute it to the Beato Angelico!!! (note 2). It was the Brunelli to publish in 1901 the Pope's Brief of Clemens VII, where stated how and why the painting was in Cagliari : it had been stolen from the Pope's room in 1527 during the Sack of Rome : ... sed etiam quandam tabulam depictam, pietatis Domini Nostri Jesu Christi et Beatae Mariae Virginis in medio, in portulis vero illam claudentibus hinc Beatae Annae Virginem filiam in manibus tenentis, inde autem Beatae Margaritae imagines devote egregieque pictas habentem quamut accepimus, Joannes Barsena miles Caesarei exercitus, a cubiculo et camera nostra abreptam, primo in monasterio Sancti Augustini extra muros Civitatis Calaritanae dimissam, mox voluit ut in sacristia tuae Ecclesiae Claritana et per te custodiretir et ad nos mitteretur, etiam concedimus, et tibi tuaeque ecclesiae calaritanae auctoritate apostolica tenore presentium perpetua donamus." (note 3)
The spanish soldier, Joan Barsena that under orders of Connestabile Carlo of Borbone took part with the Lanzichenecchi and some italian soldiers, to the famous Sack of Rome, while he was going back to his country he had to stop in Cagliari, after a ship wreck. Being afraid that this was a sign of the wrath of God, he left the painting with the Augustinians of this town. The archbishop Girolamo of Villanova, informed the Pope of the painting, gave it to the cathedral as a gift with the Brief of July 23rd, 1531, where there was obbligation of exposition, every year during the Assumption celebration :"... semel in anno in singulis Assumptionis Beatae Mariae Virginis festivitatibus, secundis vesperi Honorifice ac devote astanti populo ostendi"(note 4). The Brunelli was the first to direct the research in the flemish painting, attributing the painting to Gerard David (note 5) then the Scano (note 6) and the Aru (note 7) that dated back the central table model to a prototype of Van Der Weyden, from whom David had taken it, dating the composition in the first ten years of the 16th century.
The Aru, even seeing the different style prefers to think the painting author is David, debtor to Van Der Weyden from which he copied it, of the central table. He considers the fact that this kind of composition, with the busts of Our Lady of Sorrows and the dead Christ, in two tables close together or just one table exist in different riproductions and two of them are in the Strasbourg and Bruges museums, they are the same as ours. Even if considering the one in Cagliari at a higher level than the others, he thinks of a common derivation from an original of Ruggero already desappeared. Aru's supposition has been also accepted by Delogu (note 8), Maltese and Serra (note 9), whereas Chastel talks about the painting as a quite modest thing (note 10). Starting with this attribution problems, it was decided to submit the painting through tests that would be useful for the restauration and to solve the problems of the paternity of the work. We had some good results, as it was said, and we will talk about them starting with the radiographies, that allowed to see the structure well and the woodden support and state of preservation. The support of the two side

tables is made of two oak boards, cut in a radial way, glued where they fit together without other joining points. The frame isn't put on, but it is carved in the boards wood and in it there are ancient nails (short and thick) and modern ones (long and thin). The wood, beside some holes cau sed by woodworms, is kept in good conditions. The central panel support in the other hand, is formed by three boards, they are probably in oak too, cut in radial way, connected and supported by four pegs, the mone- ding frame isn't carved in the same wood board, but it is inserted on the support and it is composed of six pieces inserted one with the other, so we can see the first difference among the two side tables and the central one. The wood is kept, here also, in good conditions, beside some spare holes due to woodworms. With the infra-red researches it has been pos- sible to see the drawing under the panels and it has cleared what the ra diographies showed underneath. There are two kinds of drawing on the left table : one is at long and thin intervals, with charcoal stck, the oth is at short and thick intervals with goose feather and pigment (see pictu- re 2). The lines are parallel and don't create any shades but they are just to outline them, so the clothes pleats are represented by parallel li nes that meet in an angle. There are differences between the drawing and the final version : a face profile with drawn hair locks that goes down upright along S.Ann's face (picture 3) the chin is more interior, changes of mind are shown on the Virgin's face (picture 4) and hands, as in the Child's hands and S.Ann's too. With the RX are shown some se- cond thoughts : the Virgin in the first version was with her head in a higher position and her mouth was wider and fleshy also in the right tabl we find the same kind of drawing without noticing changes according to th final version. Very much different from the two tables we find the prepa tory drawing in the central panel : it is very fine especially in the face (pictures 5-6), at short very light intervals, extrimely delicate, then it gets stronger in Our Lady and Christ's hands (picture 7). The blood that gushes out from Christ's injuries has been drawn, but the pictorial ver- sion hasn't followed the drawing. The right hand's little finger is a bit moved up according to the final version, the same thing for the ring fin- ger. Also the hair has been drawn. The work has been done with goose pen and pigment. The difference between the side tables isn't only in the intervals, but above all the drawing idea: in the central panel, in fact, is used to create shades as we can see on the faces complexion and on Christ's neck, a very fine network that gives chiaroscuro. The drawing idea of who did the other two tables, is at the opposite, strictly line. We can see again very clearly through the radiographies a complexity of dra pery on Our Lady of Sorrows' mantle (picture 8). The azurite got darker because of the yellowing of the oily link that does not permit a correct reading of it, which we don't absolutely find in the characters of the two side tables. Another thing that differenciates the other two tables is the "craquelure". Through RX we can hardly see craquelure in the central panel. On the Our Lady of Sorrows' mantle is a bit more marked. Avery heavy craquelure on the whole surface is in the two side tables (picture 9-10). In order to finish, some samples (not bigger than a micron) have been taken in the parts shown in the drawing here aside) and submitted to microchimical, physical and quality of colours tests with microscope, to identify the materials. All the samples portions have been consolidated with polyester resin, sectionned and smoothed to obtein stratigraphic mi- crosections to be scrutinized at the microscope in visible reflected light conditions and at ultra violets. The interpretation is the microphotogra- phic documents result enclosed and the observations through the micro- scope. The samples have been done as it follows :

Pic.3 - Left table
Reflectography I.R.
S.Ann's face

Pic.4 - Left table
Reflectography I.R.
Virgin's face

Left table

1) The Virgin's neck complexion (in connection with the table's crack)
2) Gold from the bottom over the Virgin's head (in connection with the ta ble's crack)
3) Red from the Virgin's sleeve dress (in connection with the table's crack)
4) Navy blue (dark blue) of S.Ann's mantle

Central panel

5) The Virgin's hand complexion
6) Dark blue in the Virgin's mantle lower part.

Right table

7) Green from the dragon shape

8)Blue from S.Margaret's mantle under her left elbow (in connection with the table's crack
9) Red from S.Margaret's clothes on her left elbow (in connection with the table's crack).


Pic.5 - Central panel Picture I.R. Our Lady's face

It will be enough to do general considerations that we reached after testing . The preparation is composed by calcium carbonate plus proteinic links, animal glue layed in considerable thickness. There are not many considerable differences among the tables, just in the central panel preparation the glue is layed continuously and evenly. The glue is layed in an irregular way in the two tables : more clotted and thick in some areas, more liquid in others.
In the priming are shown layers of white led and oily links in various samples, as a local priming in the meaning of first pictorical version, as shown in the central panel, where the white lead under the azurite of the Virgin's mantle, is put to give volume, plastic sense to the pleats, or in the right table the white lead under the St.'s blue mantle, is to support the azurite general tune. In the other samples (as in S.Margaret's red clothes) there is no priming. It can be a casual fact or a painter's choice in order not to tune down the red pigment brightness. For what may concern the pictorical layers, the pigments found in the samples (azurite, cinnabar, madder lacquer, brown earth, gold, white lead, black) are in tune with the flamisch painters' way of working in the 15th-16th century.
The layers' structure is simple. The touches of the brush form rather thin thickness. In sample 3 and 4 the blackish traces are to show the drawing underneath, noticed from the photographic and riflectographic I.R.researches. The tests done show the varnish is not homogeneous, sometimes it can hardly be seen, sometimes with yellowish fluorescence, sometimes with greenish fluorescence; all this gives hard time trying to discover the original layers. It looks like some parts have been deliberatelly coloured, it is difficult to say if this happened at the very beginning or during partial restauration. In the pictorical version we noticed some eveness in all the tables : the pigments are put down with short and adjacent touches, forming very thin layers of some micron wide. There has been colour superimposition: at the bottom gold on red bole (obviously) and, on S.Margaret's clothes red lacquer on cinnabar, which is flemish usual veiling (very thin wash of colour) technique.


Pic.6 - Central panel Picture I.R. Christ's face

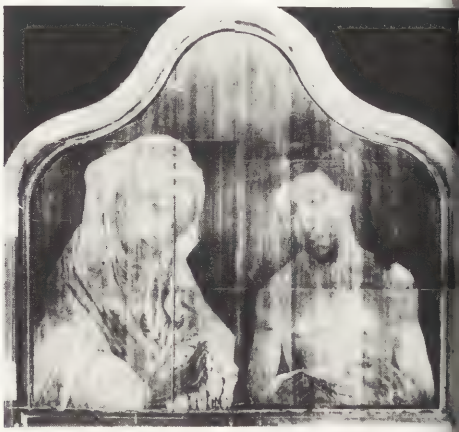
From the X Rays we can see on Christ's complexion, two later layers of colours : one before the hair was painted and one afterwards, to define the detail. In the left table the pigments composition is different, over all, for the cinnabar white lead of the complexion: it looks like there is more of the second one.
There are big quantities of varnish (probably even the original one) that is oxidized rusted with brown yellowish spots of changing sizes and intensity, particularly shown on the complexions.
A lot of wax drippings on the whole painting have taken away varnish in some parts, without damaging the colours, anyway, and showing the brightness.
The pictorical surface shows fallen colour and preparation along the joining of the two tables of the left table (the Virgin's face) and in the right one, on S.Margaret's neck and sleeve, and also along the boards joining. In the central table ther have been fallen of colour and preparation too, due to the actions of sharp objects (picture 11). Up on the right area two fallen of colour and preparation have been stuccoed and integrated with neutral paint (picture 12).
The azurite of the Our Lady of Sorrows'mantle and S.Ann's too, got darker because of the yellowing oily links. The gold from the bottom is thin and fragmented. The frame lost a lot of gold in all the tables. But, after all, the pictorical surface(beside some missing parts) is in good condition. The tables are in fair conditions, with some holes due to woodworms.
All these damages haven't compromised this work of art, anyway, but it surely needs restauration to bring it back, as much as possible, close to the original one. This seems to be possible because, still existing the original varnish, it excludes that real restauration and deep cleaning have been done. The surface dark colour, due to the yellowing of the frames and of the links, but above all the dirt and candles'smoke, shouldn't be a very big problem : after the cleaning the colours should go back as they were at first.
At the end, we can say we found out some things to make it all clearer : there are differences between the two side tables and the central one, that make us understand this tryptych does not belong to just one author and

being David, or considering David as the author of everything except the central panel which is probably a copy from Van der Weyden. The last word on this question can be said as soon as the restoration will be over at the present time we can only say this : all the three panels are original, painted in two different times and by two different authors; the central table is older than the side ones, and it was rectangular shaped at first; later it got the shape we can see with the present frame and this is all, probably at the end of the '400 or at the beginning of the '500. Can the author be Van der Weyden ? But unluckely comparing the results at Infra-red of other Van der Weyden's works, it doesn't help very much as C.Perier D'Ieteren says : "L'etude du dessin sous-jacent de Van der Weyden, comme celui du Maitre de Flemalle, en est encore a ses balbutiements. En effet, fort peu de documents infra-rouge ont été publiés jusqu'à ce jour et l'étude des oeuvres autographes du maitre est faussée par des comparaisons abusives avec des tableaux d'attribution contestée" (note 11).

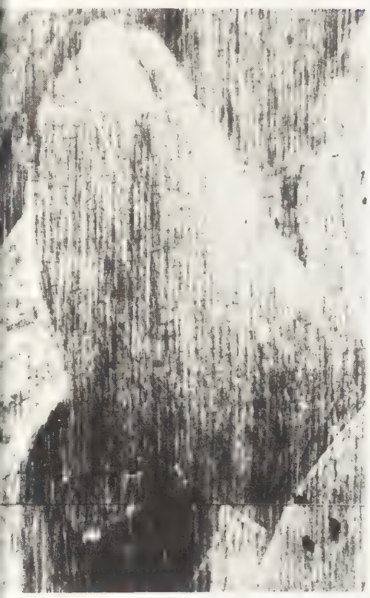
The painting level is surely very high; the Our Lady of Sorrow's face typology, the dropery treatment, the delicacy and care of the presentation of the details, the sorrow representation espressed with great measure : all this is Rogeresco. For what may concern the side panels, David's name as the author is the most appropriate, but it is necessary to make clear that the Child on the left wicket door is the same as in a painting of the "Maitre au Feuillage brodè", Ruggero's follower, kept in the Palais aux Beaux Arts of Lille. And beside this, the IR photographies of this painting show a kind of drawing very close to ours.

We can finish with these suppositions, waiting for the restauration which will give us a better reading of this work of art, postponing to a second pubblication also including the results of the restauration, for a word we hope definite on this very beautiful and not estimated painting.

Pic.7 - Central panel
Picture I.R.
Our Lady's hands



Pic.8 - Central panel
Radiography



Pic.9 - Right table
Radiography
S.Margaret's hands

Pic.11 - Central panel
Grazing light photo of the central area
down below

ic.10 - Left table
Radiography
Virgin's face

Pic.12 - Central panel
Grazing light photo of the up right area

Pic.1 - Flemish triptych of "Clemens VIIth"
Oil on wood, XVth century
Cagliari Treasure of Cathidral

NOTES

1) P.Valery, Voyages en Corse, a l'Ile d'Elbe, et en Sardaigne, Paris 1837, p.175.

2) G.Spano, Bullettino Archeologico Sardo, VII, 1861, p.139.

3) E.Brunelli, Un trittico di Gerard David sottratto al Vaticano nel 1527, l'Arte, IV, fasc.XI-XII, 1901, pp.419ss.
It represents the Our Lady of Sorrows and Christ's Pity in the central area. In the right table (for who looks at it S.Margaret and the dragon; S.Ann, the Virgin and the Child in the left table.

4) E.Brunelli, cit., p.420.

5) The Brunelli says the composition has been done in the first ten years of the '500. This can be accepted for the wicket doors but not for the central panel. R.Serra states that it is very strange that such a clever man, Brunelli, did not realize the archism of the composition if it had been done at the beginning of the XVIth century.

6) D.Scano, Note d'arte sul Sacco di Roma, Mediterranea, Luglio 1927, p.12

7) C.Aru, Il trittico di Clemente VII° nel Tesoro del Duomo di Cagliari, Melanges Hulin de Loo, Parigi 1931, pp.16 ss

8) R.Delogu, Scheda di catalogazione, Archivio Soprintendenza BB. AA. AA. AA. e SS. di Cagliari e Oristano.

9) R.Serra, Scheda n°83, in Maltese, Arte in Sardegna dal V° al XVIII sec., Roma 1962, pp.207-208
C.Maltese-R.Serra, Episodi di una civiltà anticlassica, AA. VV., Sardegna, Milano s.d., p.322.

10) A.Chastel, Il Sacco di Roma, Torino 1983, p.75
"It was a flamish triptych, given to a chapel as they exist in big quantities. The central panel is Rogier Van der Weyden's style, the wicket doors are Gerard David's style So a very modest work that the Cardinal of the Medici must have bought in Flanders, during a journey with his cousin Leone Xth".
No doubt, this scholar has not seen the original work, but just a bad copy of it.

11) C.Perier D'Ieteren,
Colyn de Coter et la technique picturale des peintres flamands du XV° siecle, Bruxelles 1985, p.26.

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A.Chastel, Il Sacco di Roma, Torino 1983, p.75.

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Collection Le dessin seus-jacent dans la peinture. Colloque I-V, 1975-1984. Documents de travail 10-11-13, Institut Supérieur d'Archéologie et d'Histoire de l'Art, Louvain-la-Neuve, 1979, 1981, 1983, 1985.

C.Perier-D'Ieteren, Colyn de Coter et la technique picturale des peintres flamands du XV^{e} siecle, Bruxelles 1985, p.26.

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PHOTOS by : E. DI. TECH. S.r.l. Firenze

Working Group 20

Glass, Ceramics and Related Materials

Verres, céramiques et matériaux apparentés

TRIENNIAL OVERVIEW

Coordinator
Norman H Tennent
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PROGRAMME 1985-1987

The main thrust of the programme has been the various problems associated with excavated material, particularly that from underwater sites. Active members of the Working Group include those involved with the scientific examination and conservation of finds from several wrecks: The Mary Rose, The Amsterdam, The St George, and many ships wrecked off the Australian coast.

This is a field of conservation where little has been published. Conservators are faced with the problem of having to deal with material whose deterioration and conservation have not been at all well investigated. Methods of treatment prior to consolidation and the methods of consolidation themselves are poorly understood. Both these subjects are addressed in papers which stem from the triennial programme of research.

The interface with certain other Working Groups is very close, and the application of polymers as protective or decorative coatings, as adhesives or as consolidants to glass and ceramics has much bearing on the work of the Group "Resins: Characterisation and Evaluation". Papers dealing with these subjects arise from this aspect of the triennial programme.

The lack of a Group Newsletter has meant that communications between members of the Group have been minimal in the past triennial period. For a fledgling group this is particularly important, and a priority for the forthcoming triennial period should be the dissemination of a regular Group Newsletter.

MATERIALS FOR FILLING AND RETOUCHING CERAMICS - HIDDEN DANGERS

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MMARY

lot of work is put into e evaluation of synthetic terials for use in the nservation of all types of tiquities. The tests are rried out on each material isolation, whereas terials are very often ed in combination. For stance they are always in ntact with at least a all section of the object is the case for adhesives. is can lead to problems of celerated deterioration if e adhesive and the bstrate are reactive. In ramics conservation fill- g and retouching normally volves a combination of nthetic materials. For a lling the repair will be de using a filler, ssibly mixed with a lour, overpainted with a terial to simulate a aze. The glaze material y contain powder, or her type of colourant, and matting agent.

this paper accelerated llowing of a repair to a rd paste porcelain figure reported. The materials volved in making the pair were previously found have reasonable light ability, and were there- re considered suitable for e in ceramics conservation. wever when they were used combination yellowing curred very rapidly. The use of the yellowing has en investigated and entified by a process of duction and experiment.

Introduction

During the last 18 months a number of materials have been investigated for use in ceramics conservation work. This work has been carried out using test methods previously described (1). The tests involve the assessment of each material in isolation since it is not normal procedure to combine materials in the tests. However the materials are normally used in a situation where they are in contact with the fabric of the object, or mixed with other materials prior to use, or painted over other materials. In ceramics conservation the latter two cases are common when filling and retouching work are carried out.

When a gap fill is made, a synthetic material such as an epoxy putty or a polyester filler is often used. This has to be coloured and finally coated with an artificial glaze. This combination of materials resulted in unusually quick yellowing of a repair when an object was returned to storage following conservation. The object involved was a biscuit ware figurine of a shepherdess. The cause of the yellowing was investigated using tests which evaluated the performance of the main materials used in the repair.

Repair of a Biscuit Ware Figurine of a Shepherdess

The figure of a shepherdess, registration number AF 3234, had a section of the hat brim missing. The ceramics conservation section was asked to restore the figurine. The brim was remodelled in Milliput epoxy putty. A rough model of the brim was prepared and positioned on the hat using the epoxy itself as the adhesive. Whilst the repair was wet it was smoothed by rubbing the surface with a finger wetted with distilled water. In this manner the bulk of the shaping and smoothing was achieved in situ. When the epoxy putty had hardened the shaping and smoothing was completed using garnet paper, grade 7. Fine surface filling was carried out with ICI cellulose stopper. Once the shaping and smoothing was satisfactory the repair was painted with Rustin's Clear Plastic Coating, a two component urea formaldehyde lacquer mixed with Winsor and Newton's dry ground artist pigments to match the colour of the object and a matting agent, Gasil 23C. Final surface finishing was achieved by rubbing the surface with Flexigrit, a fine aluminium oxide abrasive paper.

On completion of the conservation work the figurine was returned to a ceramic storage area. This consists of floor to ceiling wall cases with glass fronts. There are skylights in the roof over the area which is also lit artificially because it is used as a study area for the collection. The figurine was left in this store for five months. On removal the repaired area was found to have yellowed, and a water mark type stain had developed in the biscuit ware around the repair.

All of the materials used in making the repair had been used previously in the Museum and by private restorers. Such quick discolouration had not been reported previously.

Investigation of yellowing

1. Experimental

The effects of light and of dark, heat, ageing on the main materials alone and in combination were investigated.

1.1. Preparation of samples

A film of Rustins Clear Plastic Coating was prepared by mixing the two components according to the manufacturers instructions and painting the mixture onto a polythene sheet. After curing, the film was peeled from the polythene.

Samples of Milliput Epoxy Putty were prepared by mixing the two components according to the manufacturer's instructions. The mixture was then spread onto glass slides and the surface smoothe with a finger wetted with distilled water.

Combined samples were prepared by painting Rustin's Clear Plastic Coating onto the surface of samples of Milliput Epoxy Putty prepared as described above. These samples were used in light an dark ageing tests.

To investigate the cause of the water mark type stain on the biscuit ware around the repair, samples of Milliput smoothed with water were prepared on an unglazed tile and, after curing, Rustin's lacquer was painted onto the surface of the Milliput.

For comparison purposes an epoxy putty was prepared in the laboratory using Araldite MY753 and Hardener HY956 mixed with kaolin (filler) and titanium dioxide (colorant). Samples of the putty were prepared on glass slides and coated with Rustin's Clear Plastic Coating. These samples were used in dark ageing tests.

1.2. Light ageing

Light ageing was carried out using a Microscal Light Fastness Tester equipped with an MBTL lamp. Samples of the materials were mounted in water cooled cells suspended around the lamp. The samples were exposed to the lamp until either yellowing occurred or enough time had elapsed for the samples to be judged stable under the ageing conditions. For this type of light fastness tester the exposure needed for Paraloid B72 to discolour, 2500 hours, has been taken as a measure of stability.

1.3. Dark ageing

Accelerated dark ageing was carried out at 70°C in an oven. The samples, prepared as described, were exposed until yellowing occurred or 28 days had elapsed.

1.4. Monitoring Colour Change

To follow colour change the UV-Visible spectrum of the Rustin's lacquer was determined before and after light ageing and dark ageing. The spectrum of the Milliput samples could not be observed because the samples were opaque solids. Yellowing was observed by comparing the colour after ageing with an unexposed control sample.

2. Results

2.1. Light ageing

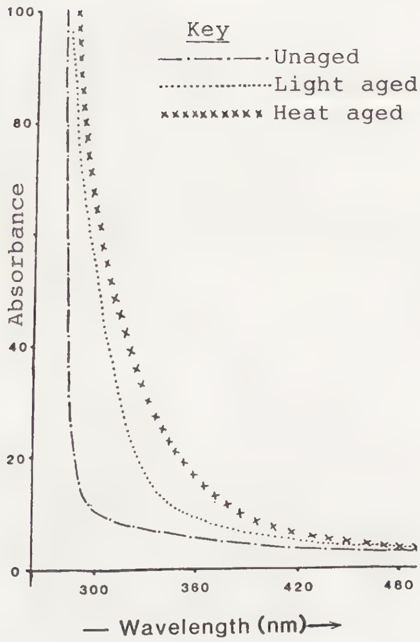
The Rustin's Clear Plastic Coating started to yellow after 2548 h in the light fastness tester. The spectra before and after agein are shown in Figure 1. Thus the material had a similar stability to light as Paraloid B72.

The Milliput sample and the sample coated with Rustin's lacquer showed no discolouration during light ageing.

2.2. Heat ageing

The spectrum of the Rustin's Clear Plastic Coating after 28 days at 70°C is shown in Figure 1. The coating started to yellow after 6 days in the oven. The yellowing occurred much more rapidly than has been observed for other synthetic materials evaluated by this group.

The Milliput sample became pale yellow within 28 days. The Milliput samples coated with Rustin's Clear Plastic Coating and prepared on both glass and tile substrates yellowed very rapidly, this taking less than a day to occur. In both cases, as well as the surface of all of the samples yellowing rapidly, a darker yellow water mark had developed towards the edge of the samples. In the case of the samples on the tile substrate the water mark had extended into the tile.



The coated samples made from epoxy putty prepared in the laboratory had yellowed within 10 days, consistent with the rate of yellowing observed when Rustin's Clear Plastic Coating was age

at 70°C. This suggested that a component in the Milliput which was mobile, if not soluble, in water was causing the increase in the rate of yellowing.

3. Discussion

Although the Rustin's Clear Plastic Coating discoloured after 2548 hours exposure to the MBTL lamp, this degree of exposure prior to yellowing was greater than has been observed for many other synthetic materials. Thus the material could be described as stable with respect to light. Neither Milliput or Milliput coated with Rustin's lacquer discoloured during light ageing indicating that the materials should be safe for use in the restoration of ceramics. However the samples all yellowed during dark ageing at 70°C. The Rustin's sample yellowed after 6 days, a sample of epoxy putty prepared in the laboratory and painted with Rustin's became pale yellow after 10 days, the Milliput yellowed within 28 days and the Milliput coated with Rustin's sample yellowed in less than 24 hours. These results suggested that yellowing was more likely to occur if Milliput Epoxy Putty and Rustin's lacquer were used in combination and were kept in dark or low level light conditions. It also seemed probable that a reaction between the urea formaldehyde lacquer and a component of the Milliput epoxy putty was occurring and causing the rapid yellowing.

An examination of the area where the figurine was stored following conservation revealed that the cases were not lit directly and indeed even during the daylight hours light levels inside the cases were low. Also there was no artificial light in the area during weekends and on week days the lights were only switched on when the area was in use for study. Thus an explanation for the rapid yellowing of the repair on the figurine was that Rustin's lacquer on top of Milliput Epoxy Putty was incompatible especially when stored in dark or poorly lit conditions.

Similar yellowing of materials containing an anti-oxidant had previously been observed in the laboratory. These materials had been analysed (2) and the anti-oxidant, butylated hydroxy toluene (BHT) had been identified as a component. The observed behaviour of the Milliput/Rustin's system was similar to the behaviour reported for BHT. The yellow material was extracted from the aged samples, but the IR spectrum obtained was not identified.

BHT is a white crystalline material which oxidises and turns yellow colouring other materials with which it is in contact. A review of the literature on the yellowing of BHT (3) reports that the structure of the oxidised molecule has not been elucidated, but various workers have agreed that the oxidised form is yellow and that the yellow colour can be reversed by exposure to a strong light source.

To evaluate if BHT could be the cause of the yellowing a small quantity of BHT was mixed with a sample of the putty prepared in the laboratory described under 1.1. above and the samples dark aged. The samples yellowed rapidly.

This indicates that a component other than the filler and colourant in Milliput Epoxy Putty reacts with the urea formaldehyde lacquer under dark ageing conditions, and that the component is probably an anti-oxidant, possibly BHT.

A further test was carried out. Samples which had yellowed during ageing at 70°C were exposed to the MBTL lamp. After 14 days exposure to the lamp the colouring had been reversed, behaviour consistent with that reported in the literature for BHT.

4. Conclusions

Tests can be carried out to determine the stability of materials towards light and heat (dark) ageing and to assess their reversibility, shrinkage and change in flexibility and strength. Such tests have been shown to be useful in making a selection of materials for use in conservation. The tests are normally carried out on the materials in isolation although materials are often used in combination with other materials. The mixing of two apparently suitable materials can result in an unexpected deterioration in the properties of both materials.

For the repair of the biscuit ware shepherdess described, the use of Milliput epoxy putty and Rustin's Clear Plastic Coating in

conjunction resulted in rapid yellowing which had not previously been observed. The fact that the figure was an almost pure white colour and that the repair had been coloured to match the biscuit ware enhanced the effect of the yellowing. The investigation of the phenomenon suggested that the rapid yellowing was caused by the presence of an anti-oxidant, possibly BHT, in the epoxy putty reacting with the urea formaldehyde lacquer.

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(2) Chaston, S.H.H., Daniels, V.D. and Pascoe, M.W., Report on Haggerty's Silver Keeper-BM, Department of Conservation Internal Report, December (1978).

(3) Smeltz, K.C., Why do white fabrics and garments turn yellow during storage in polythene bags and wrappings? Textile Chemist and Colourist, Vol. 15, No.4 (1983) pp. 17-21.

Acknowledgements

The authors are grateful to Janet Clougherty of the British Museum Ceramics Conservation Section for bringing the problem to their attention and to Vincent Daniels and Andrew Oddy for reading the manuscript.

Suppliers

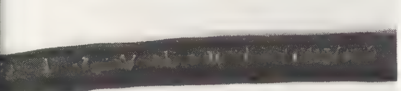
Milliput Epoxy Putty: The Milliput Company, Unit 5, The Marian, Dolgellau, Gwnedd, North Wales, LL40 1UU.

Rustin's Clear Plastic Coating: Rustin's Ltd., Waterloo Rd., London NW2.

UMMARY

rom the middle of the seventeen-
h century to the middle of the
ineteenth century, glaziers in
ngland often marked their lead
ames with an identifiable symbol.
ourteen of these marks were
ound on a restored sixteenth
entury window in the Burrell
ollection in Glasgow when it
as taken off display for
onservation in 1986. The study
f these marks has proved
nvaluable in helping to piece
ogether the history of the
indow.

IG.1 : Joachim and Anna.
urrell Reg. No., 45/ 389



IG.2 : "OLIVER 1802"

LEAD MILLING MARKS FROM A SIXTEENTH CENTURY STAINED GLASS WINDOW

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Introduction

Stained glass windows are composed of two basic materials; glass and lead. Much research has previously been devoted to the study of glass, but as yet relatively little has been written about the lead. This report results from the conservation of an early sixteenth century French stained glass window in the Burrell Collection in Glasgow. (FIG.1) This panel depicts the meeting of Joachim and Anna, the parents of the Virgin, at the Golden Gate in Jerusalem. Prior to conservation the window had obviously been restored and releaded, although no record of any work done to it was known to exist. Very little of its history had been documented, and some of that was inaccurate. (*1) Due to the delicate condition of the lead, and the extensive damage sustained by the glass since its previous restoration, a thorough and complete releading was necessary. During conservation much valuable information was revealed as a direct result of close examination of the lead cames.

Conservation and Documentation

Before the old lead was removed, a rubbing was taken over the entire window using cartridge paper and heelball. On this was recorded the various lead sizes, and any peculiarities about the construction of the window which would be valuable information when releading.

As the window was dismantled and each piece of glass removed, the old lead was cleaned immediately by brushing the inside (the heart) with a stiff bristle brush to remove the old, crumbly putty. Any remaining dirt was wiped away using an acetone swab. (It was useful to do this prior to cutting each strip of lead, thus avoiding cutting through any interesting marks.)

The majority of the leads which made up the window were 3/16" (5mm) wide, hand milled, round came. On one side of the heart was stamped the glazier's name and date of manufacture, "OLIVER 1802". (FIG.2) The overall length of the inscription was $2\frac{3}{8}$" (60mm). This inscription was repeated every $4\frac{1}{4}$" (108mm) along the length, interspaced by twelve tooth marks, including the ones on either side of the inscription. The gap between each tooth mark varied slightly, but on average there were five teeth every twenty millimeters (5 / 20mm). From the length of the repeat we know that the diameter of the milling wheel must have been $1\frac{5}{8}$" (34.5mm).

```
          ←———————— repeat length 4¼" ————————→
. . I I I I O L I V E R I 1 8 0 2 I I I I I I I I I I I I O L I V . .
          ←——inscription ——→
```

The reverse side of the lead had no inscription, apart from the milled tooth marks which were similarly spaced to those on the other side.

A total of fourteen different types of lead were cleaned and recorded in a table, giving details of any identification marks, width and height of lead cames, spacing of teeth marks, wheel diameter, date of manufacture, and glazier (if known). (FIG.3)

Two other charts were drawn up;

1. (FIG.4) shows where each different type of lead came from within the structure of the window prior to conservation.

2. (FIG.5) shows, by using conventional symbols, which pieces of glass came from the original sixteenth century window, and which were restorations.

By laying FIG.5 on top of FIG.4 it became obvious not only <u>when</u> all the restorations had been done, but also, in some places, <u>by whom</u>. This information could not have been so accurately recorded by looking at the glass alone.

The practice of naming and dating leads was common from the middle of the seventeenth century until the beginning of the nineteenth century when it gradually died out due to the introduction of machine milled lead, bought in bulk from independent manufacturers. (*5) Some workshops today still carry out the practice of melting, casting, and milling their own lead, however, the milling wheels are industrially made and are devoid of any identifiable marks. It has been suggested that the necessity of these glazier's marks was for taxation purposes, but this has still to be verified. (*6)

LEAD MILLING MARKS FROM A SIXTEENTH CENTURY STAINED GLASS WINDOW (cont.)

IDENTIFICATION MARKS	SYMBOL	REPEAT LENGTHS	WHEEL DIAMETER	SPACING OF TEETH MARKS	LEAD WIDTH AND HEIGHT	DATE OF MANUFACTURE	GLAZIER (IF KNOWN)
3/16" OLIVER 1802		$4\frac{1}{4}$" (108mm)	$1\frac{5}{8}$" (41mm)	5 / 20mm	5 / 4.5 / 2mm	1802	OLIVER
3/8" OLIVER 1802		$4\frac{3}{4}$" (121mm)	$1\frac{1}{2}$" (38mm)	5 / 20mm	8.5 / 4 / 2.5	1802	OLIVER
1/8" OLIVER 1806		?	?	5 / 20mm	3 / 4 / 2	1806	OLIVER
3/8" OLIVER 1806		$4\frac{1}{8}$" (105mm)	1 5/16" (33.5mm)	4.5 / 20mm	9 / 4.5 / 2.8	1806	OLIVER
1/8" x		?	?	48 / 20mm	3.7 / 5 / 3	c. 1900	DRAKE ? (*2)
3/16" x		$4\frac{1}{2}$" (114.5mm)	1 7/16" (37mm)	48 / 20mm	4.5 / 5 / 3	c. 1900	"
1/4" X		4" (102mm)	$1\frac{1}{4}$" (32mm)	32 / 20mm	6 / 7 / 4	c. 1900	"
1/2" X		4" (102mm)	$1\frac{1}{4}$" (32mm)	32 / 20mm	12.5 / 7 / 4	c. 1900	"
3/16" O		$4\frac{1}{4}$" (108mm)	$1\frac{5}{8}$" (41mm)	4.5/20 "O" 3/20 reverse	4.8 / 5 / 2.5	c. 1800	OLIVER ?(*3)
3/8" W		?	?	4 / 20mm	9 / 4.5 / 2.8	c. 1800	WARRINGTON ? (*4)
5/16" OLD MILLING		–	–	13 / 20mm	10 / 4 / 2.5	18th C. ?	?
1/8" DIAGONAL MILLING		–	–	20 / 20mm	1.8 / 3 / 2	20th C. ?	?
1/8" NO MILLING		–	–	–	3 / 6 / 3.5	20th C. ?	?
1/4" NO MILLING		–	–	–	6 / 7 / 4	20th C. ?	?

FIG.3 : Table giving details of the fourteen different lead types found in the window prior to conservation.

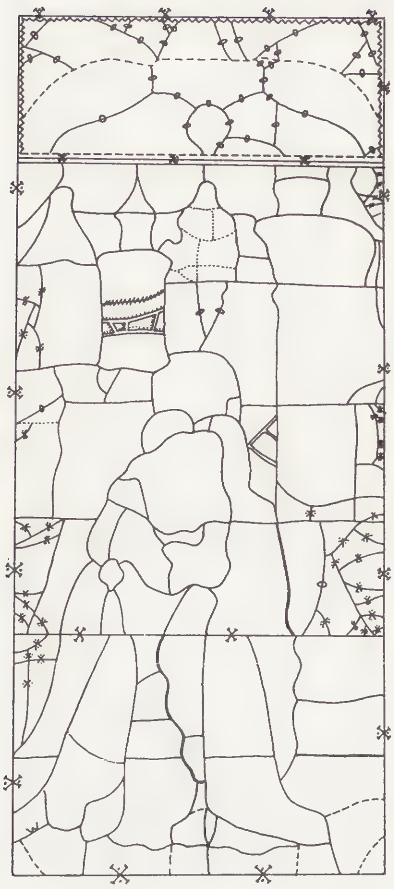

FIG.4 : Diagram showing position of leads in window prior to conservation. (See FIG.3 for explanation of symbols.)

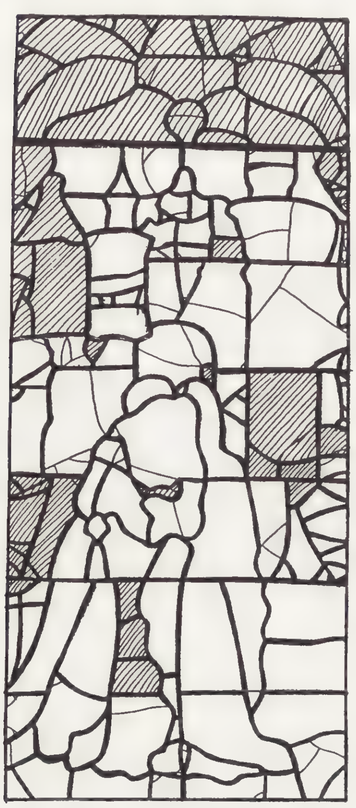

FIG.5 : Restoration Chart. Clear areas denote original sixteenth century glass. Shaded areas denote restoration, prior to conservation.

Conclusion

The close examination of both the lead and the glass from this particular window has revealed vital information in helping to piece together its history. Comparatively little is known about the glaziers who were working from the middle of the seventeenth century to the middle of the nineteenth century. This research has helped to throw some light upon the activities of some of those men who were working at that time. Hopefully further studies of lead and lead cames will contribute towards a fuller understanding of the history of stained glass.

The author would be very interested to hear from, and exchange information with, anyone with a similar interest in lead cames.

NOTES

1. Maurice Drake, The Costessey Collection of Stained Glass, (William Pollard and Co. Ltd.), 1920, p.16, no.62.

also, William Wells, Stained and Painted Glass, Burrell Collection, (Glasgow Museums and Art Galleries), 1965, p.64, no.221.

2. Several other windows in the Burrell Collection, that have recently been conserved, have had similar marks on the lead. The only known connection between them and the Joachim and Anna panel is that they all passed through Drake's workshop. Wilfred Drake was not only an eminent craftsman, but he was also Sir William Burrell's main agent and advisor in stained glass until his death in 1948.

3. The window is made in three sections. The top section is almost entirely made up with a lead which is found only four times in the rest of the window. It dates from the same period as the "OLIVER" leads, but is marked only with a single "O". It is possible that this may also have come from Oliver's workshop, but this cannot be confirmed until more "O" leads have been discovered.

4. Jean Lafond, The Traffic in Old Stained Glass from Abroad during 18th and 19th Centuries in England, J.B.S.M.G.P., Vol XIV, no.1., note 37.

also, Glass Painters, 1750-1850, J.B.S.M.G.P., Vol. XIII, no.3. "William Warrington"

This lead could possibly be from Warrington's Workshop, or that of his father. Again, unfortunately, like the "O" leads, one can only speculate until more "W" leads have been discovered.

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6. Dr. Barry Knight, Researches on Medieval Window Lead, (J.B.S.M.G.P., Vol XVIII, no.1.) 1983-4.

LEAD MILLING MARKS FROM A SIXTEENTH CENTURY STAINED GLASS WINDOW (cont.)

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THE FRIARS PARK WINDOW: EXCAVATION, CONSERVATION AND RECONSTRUCTION OF A 13TH CENTURY WINDOW

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SUMMARY

A collapsed 13th Century window, discovered during archaeological excavations in Carmarthen, Wales, was lifted using polyurethane foam. Much glass remained in the window leads but had decayed badly and was wet, opaque and blackened. The leads were in good condition. After tests with various consolidants the glass was successfully treated with Primal WS-24, an acrylic colloidal dispersion. As a result of the treatment leaded glass pieces could be safely repositioned to obtain the original window design.

Discovery

Carmarthen Grey Friars in Dyfed, West Wales, was a royal foundation dating to c1250-1280, the benefactor being either Edward I or his brother Edmund. Contemporary records and finds of expansive foreign goods on site indicate continued wealthy patronage throughout its history.

After the Reformation the Friary was sold off, part of it temporarily becoming a school, but for the rest there is ample evidence of massive plundering. Excavations in all areas of the site produced hearths dating to the early C16th, and used to melt down copper alloys and lead. Probably associated with this industrial activity was a fire, thought to be during the suppression of the house, which destroyed the Friary Infirmary. In May 1983 whilst excavating the Infirmary (1), members of the Dyfed Archaeological Trust found a collapsed window lying in the debris, and which therefore had probably been buried for over 450 years (Fig. 1).

The window had fallen in entirely so that much of the glass, though shattered, was retained in the leads. It was lying horizontally face downwards except for one corner which had folded backwards to reveal a fraction of the inside face and a tantalising area of painted glass. Overall, as found, it was triangular in shape, the maximum dimensions being roughly 60 x 80 cms (Plate 1).

Much of the leading, medieval type C, according to the typology suggested by B. Knight (2), appeared to be in fairly good condition, finely patinated with a grey surface, presumably lead carbonate. Some of the leading however was heavily corroded and it was impossible to know the condition of the central portion which was hidden by the twisted corner. However, overall, due to the largely undamaged condition of the leads, approximately one third of the original window design was visible.

The condition of the glass was rather different; it was wet, but not waterlogged, fractured and apparently opaque and blackened as is often the case with buried medieval glass (3,4). On first inspection only a few colourless sherds of glass remained transparent but the small area of inside surface visible indicated that some, at least, of the glass had been painted. Probably as a result of the fall some pieces of glass had shaken loose from their leads. These fragments were initially difficult to identify because the whole window was littered with split, burnt slate from the roof, closely resembling the decayed glass.

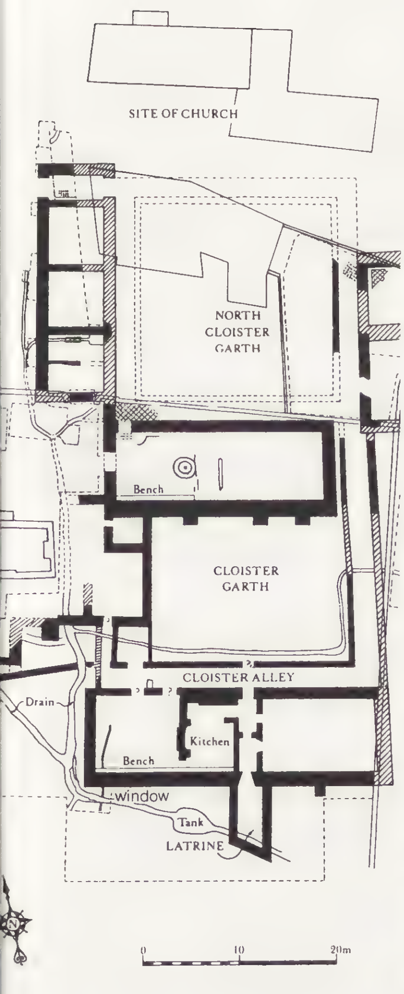


Fig. 1 : Plan of Greyfriars, Carmarthen, showing position of window's discovery.

(Plan Dyfed Archaeological Trust Ltd., Copyright reserved)

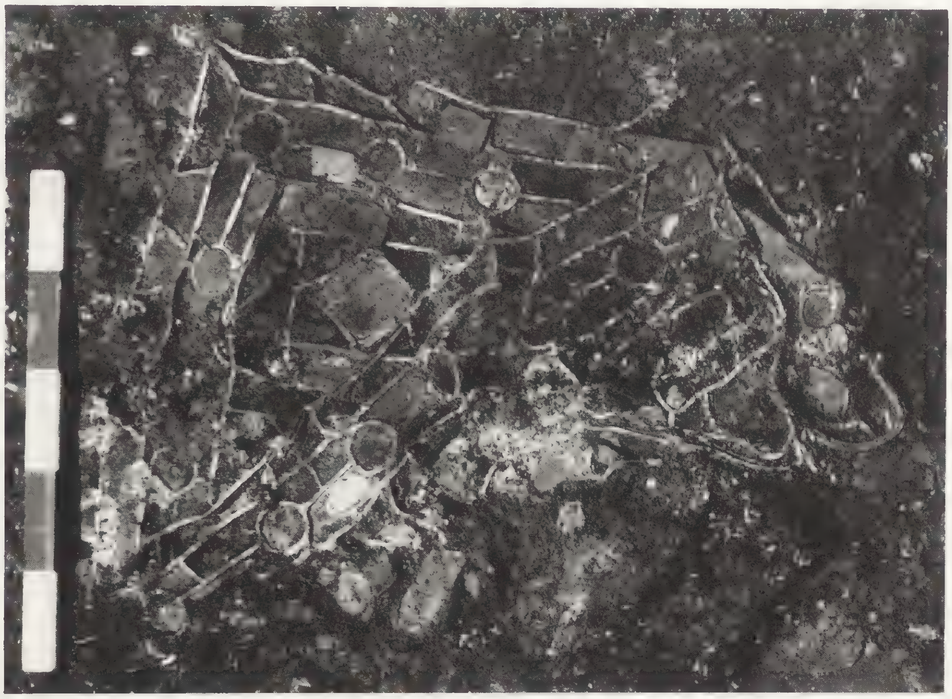


Plate 1 : Vertical photograph of the window as found, scale 50cm.

(Photo Dyfed Archaeological Trust Ltd., Copyright reserved)

The window was considered important for three reasons. First it was very unusual to find a complete medieval window by excavation. Secondly the probable date of the Friary foundation, together with the fraction of window design visible, suggested a C13th date. Little C13th window leading survives from Great Britain due to a C19th policy of releading medieval church windows. The window leads themselves were very fine. Thirdly the window was not from the church proper but from a domestic building associated with the Friary, unlike most surviving medieval windows which are in church or cathedral buildings.

Lifting

Lifting the window presented several problems. The fragmentary and shattered nature of the glass necessitated that everything be kept 'in situ' for transport to the laboratory where it could be fully recorded, but, as the glass was wet it could not be allowed to dry out without the risk of disintegration. It was assumed that the glass was of the usual medieval potash composition rather than the more stable soda-lime (5). A further complication was the need to act quickly because of the risk of urban vandalism.

Therefore the whole window had to be lifted as a block with the glass supported by the damp soil underneath. In practice this meant lifting a heavy mound of earth of about 1 metre square and 10 cm deep. The nature of the soil underneath the window was unknown at the time due to the fact it was a fire debris, but was subsequently revealed to be a slightly stony subsoil loam. Prior to the arrival of conservators on site the archaeologists had cleaned the window sufficiently to obtain its external dimensions and carry out preliminary recording, all of which reduced the time needed before the lifting process could start. Subsequent cleaning involved a fine water spray, brushes and trowels, in order to isolate the window onto a soil island. A border of about 10cm soil was left around to act as a protective edge.

As the glass was fairly shattered the use of a consolidant was considered but rejected for several reasons. As the glass was wet the consolidant would have to be water based, and the only readily available water based consolidant at that time was Vinamul 6815, a PVA emulsion, which had several known drawbacks (6, 7). It is not always easily reversible and therefore might affect subsequent treatment with other resins; it could decay to give off organic vapours which would be harmful to the leads; and application of a consolidant on site, if unsuccessful, might lead to differential drying between the upper consolidated surface and that below leading to spalling.

If faced with a similar problem again acrylic colloidal dispersions would be considered for consolidation on site. These materials are water based, have good penetrating properties due to the small particle size, and are known to be stable and reversible (6, 8). The physical disturbance necessary to lift the soil block may well have caused further damage to the window and consolidation might have reduced this. Since the acrylic dispersion Primal WS-24 was subsequently used to consolidate the glass in the laboratory perhaps treatment could have started on site. Unfortunately these dispersions were not readily available at the time of the window's discovery.

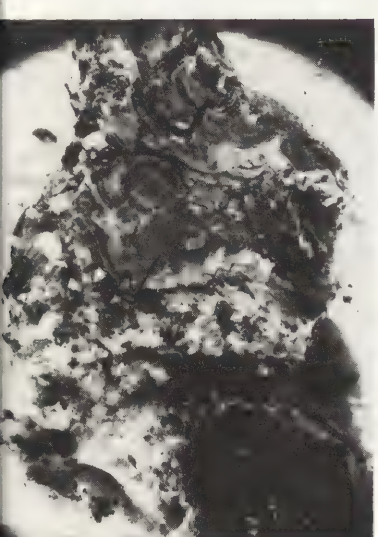
Once the window had been isolated on its matrix of earth it was then shuttered around with a wood frame and a separating layer of aluminium foil firmly placed over both window and soil as has been full described elsewhere (9). The foil also acted as a moisture retainer. The window was to be held firmly in the box by the use of polyurethane foam which had been chosen because it was strong but light, and quick-setting. The weight of the soil block together with a heavier medium like Plaster of Paris would have led to considerable difficulties for an operation which had to be quickly effected. Both materials heat up on setting but this had to be accepted as a necessary risk.

Polyurethane form contains a highly toxic isocyanate so relevant safety measures were taken.

The method of application was similar to that used by Jones (10) as described in the Conservator. Once the foam had expanded and set a hardboard lid was tacked on to form the box top and thin metal sheets pushed underneath to separate the block from the ground. Pushing a support underneath is often referred to rather matter-of-factly in the testbooks (9) but is not always easy. The pebble-rubble matrix beneath was very difficult to cut and necessitated the use of a mallet, wedge and block of wood, the whole process taking over 1½ hours.

Temporary Storage

Upon arrival in the laboratory a full programme of recording, photography and planning was undertaken before any treatment could begin, the block of soil being stored in the coolest, darkest conditions available. But the soil itself was a source of further damage via the microorganisms it contained, and as it began to dry out and shrink. It was felt necessary to move the window to some other, more stable retaining material until a programme of conservation could be instituted. Loose pieces of glass, which were no longer held in their leads were removed and stored separately on wet polyester foam in air tight boxes.



Plates 2, 3, 4 : Sherds of Medieval glass drying out over 3 hours, Magnification x 6

This still left the bulk of the glass in lead, some of which was buckled and distorted, sitting on the soil. As a temporary storage medium vermiculite, more commonly used as an insulating material, was chosen. This is a naturally occurring mineral, mostly composed of silica and magnesium oxides exfoliated to remove water. It has the advantages of being inert, cheap, easily available and most importantly water absorbant.

The vermiculite was placed in a large, flat, polythene-lined box, allowed to absorb water until it had expanded to its maximum dimensions and then piece by piece, after recording, the window fragments were transferred over. Unfortunately some sherds were too decayed to hold their own weight and so, despite all the shortcomings mentioned above several pieces had to be supported by the temporary use of PVA emulsion and fine polyester gauze. Fine particles of vermiculite were pushed underneath to give exact support corresponding to the shape of individual pieces. For nearly three years while a programme of conservation was devised and carried out, the vermiculite remained a successful, inert, holding medium. Reservations about PVA emulsion were confirmed in that it could not be fully removed from the few areas to which it had been applied, despite the concerted use of acetone, which in the absence of a large fume extractor was the most powerful solvent it was felt safe to apply.

Condition

Prior to the window's discovery the site had already produced over 300 sherds of stained and painted medieval glass some of which could be used experimentally to devise a successful treatment for the window. It was established that air drying was likely to lead to disintegration when one sherd, photographed under the microscope over a period of 3 hours, deteriorated from a wet but coherent object to a pile of "sugary crystals" (plates 2, 3, 4).

Further examination had confirmed that the condition of the surviving window glass was variable, some pieces being still largely transparent, others being partially transparent with decayed and friable edges while others were totally opaque. For the latter there seemed little chance of any detectable original colour but some sherds, if held in front of a high powered fibre optic light source, showed patches of identifiable colour, which would not be seen on a light box.

It appeared that the early stages of decay, visible before the glass became blackened and opaque, were indicated by a change in colour to yellow, lamination, and the production of black "crystals" like deposits scattered throughout the decayed areas (plate 5). These "crystals" were unidentified, but could have been reduced ferrous or manganese ions, originating either from the glass or as salts acquired from the ground. If so the yellowing was probably the initial stage of the same decay process, involving reduction of the metal ions, which resulted in black opacity. One consequence seemed to be that in partially decayed glass two colours were visible, yellow around the outer decayed edges and an original colour in the centre. It was quite possible to mistake the yellow for a genuine colour. The three glasses positively identified in the Grey Friars window were deep blue, colourless and a flashed red.

Loose and broken sherds could be orientated by two features; firstly one surface was always pitted, in the manner often described for the exterior surfaces of standing medieval windows (3, 11) and therefore could be identified as such. This also suggested that the window had been standing for some time before its collapse which added to the evidence of a relatively early date. Secondly, like all medieval window glass the quarries had been cut into shape using grozing shears (12), giving a clearly defined edge which was totally different from a shattered break. Due to the quality of the intact leads many loose quarries could therefore be assigned to identifiable places in the overall window design. Quarry edges were also marked in places by an approximately 5mm band of white decay products which were assumed to be the remnants of a "putty" originally used to place the glass in the leads but could have been the corrosion from the leads themselves. However given their generally uncorroded nature this seemed unlikely.

Choice of Treatment

For longterm stability the water in the glass had to be removed and replaced with a consolidant which fulfilled the normal conservation requirements of stability, compatability and reversibility. Ideally it should have a refractive index close to medieval glass so that partially laminated but still transparent pieces would retain their colour on drying. Lastly it was important that the resin gave off no organic decay products which might effect the leads.

Two much used resins, Paraloid B72 and Polyvinyl Acetate, (BDH M.V. 45,000), (13) were tested as possible consolidants for the wet glass, PVA producing quite good results in terms of weight and appearance for the less decayed pieces. However both resins had certain drawbacks for this application. As both were immiscible with water fractured glass had to be dehydrated through a series of water-to-solvent baths which resulted in considerable physical disruption for already friable pieces. More importantly the leaded glass

might well have disintegrated if moved from the damp vermiculite supporting it and could not therefore be safely dehydrated.

It was decided to try acrylic colloidal dispersions for the reasons outlined above, namely the facts they were water-based, stable and reversible. However like all resins the properties vary (14, 15) and not all seemed appropriate for use in this case. In the end the choice was limited to two resins which the manufacturers were willing to supply in small quantities, Primal WS-24 (Rohm and Haas) and Revacryl 452 (Harco Chemicals). Both manufacturers provided good data sheets on request. Experiments with both dispersions produced a marginally better result with Primal WS-24 i.e. in still transparent glass the colours appeared deeper. The remaining transparency of these excavated glasses was assumed to be partially the action of water, which has a similar refractive index to medieval glass, replacing constituents lost from the glass network during degradation. The water therefore not only held severely degraded sherds together but also masked the true extent of decay until a sherd was allowed to dry out. If the water could be replaced by a consolidant of similar refractive index and which fully penetrated the decayed glass this transparency should be retained. Unfortunately no suitable resin with a correct refractive index was available (16) but it was assumed that the better performance of the Primal WS-24 was due to the fact that it had impregnated the decayed glass more thoroughly. However due to the variable nature of the glass, even using photography, this was a subjective judgement.

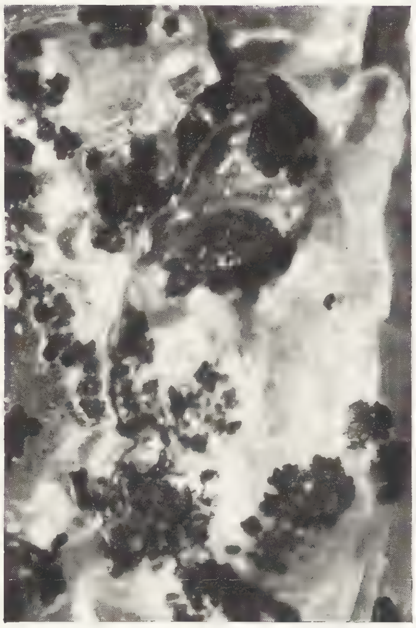


Plate 5 : Black "crystal" like deposits in decaying glass, Magnification x 20

Conservation

Treatment was as follows: pieces strong enough to be moved from the vermiculite and treated separately were cleaned on both sides with water, soft brushes, and a hand held garden water spray which proved a most useful tool. Fortunately there were no putty or mortar concretions on the glass which might have necessitated a more rigorous, and possibly destructive, cleaning, however the possible putty shadow around the grazed edges was left to show where the quarries had fitted into the leads.

After cleaning, to achieve maximum penetration by the extraction of any air introduced into the glass during the prolonged storage and cleaning process, sherds were vacuum impregnated with a 2% solution of Primal WS-24, the process being repeated with 4% and 10% solutions. It was found that better penetration, and therefore consolidation, was obtained using the dilute solution but that the overall effect after the initial treatment was an unsatisfactory, pale yellow colour, which reduced any remaining transparency. As noted above it was assumed that decayed and largely laminated glass had to be packed with consolidant to reduce the problem of light interference as the laminations dried out. After the final immersion a coat of 15% Primal WS-24 was applied for this cosmetic purpose and to act as a final protective plastic layer.

Many quarries, although broken, were complete. It was possible to join broken edges by pushing pieces together as they dried from the last immersion in Primal which therefore also acted as an adhesive. The larger and more fragile pieces were backed with a fine polyester gauze as they dried, the gauze being invisible on the front surface.

The leaded pieces lying on vermiculite were individually cleaned on the visible side only, after which solutions of increasingly concentrated Primal WS-24 were painted on as described above, ending with the 15% concentration. Once the upper side had been successfully treated, moulded amounts were constructed using fibreglass bandage (9, 17). These bandages, impregnated with a rapid setting moisture activated polyurethane, are used by the medical profession for the construction of rigid but light supporting frames. Using cling-film as a separating layer, four inch strips of fibreglass bandage were applied in alternative directions until a suitably strong support had been built. The bandage sets rapidly and so the operation is best carried out by two people. Protective gloves should be worn to prevent the resin contacting the skin. The individual pieces of leaded glass could then be turned over by slipping a flat board beneath the supporting vermiculite, and inverting the whole package.

Once turned the inner surface was similarly cleaned and consolidated in the manner described above.

Reconstruction

As the cleaning progressed numerous shattered fragments had been found to match, in particular several painted fragments fitted together to reveal a bird of prey with wings. A central quarry contained the bird, supported by two wing shaped quarried (Plate 6). This had a heraldic quality which did not seem to fit into what was otherwise a fairly geometrical design. The area under the folded corner had revealed a loose segment of leaded glass unattached to any other part of the window but whose general placement was known. By the time the glass had been stabilised about 60% of the window design had been worked out but it was doubtful whether the central portion would ever be clarified without some creative reconstruction.

Plate 6 : Three quarries depicting bird with wings.

The colours, where they survived, had been fitted into a design, and seemed to suggest that the very outer border consisted of clear glass, and the rectangular quarries in the next two rows were flashed red. Unfortunately the circular quarries found in this part of the design had decayed beyond identification. The birds and wings were outlined by a red enamel paint, painted on the inside face, but again the glass itself was totally opaque. As there was no trace of another paint it was assumed that originally the body and wings of each bird had been unpainted and had appeared the same colour as the glass quarry itself. Lastly some blue glass was still retained in the leads around the lozenges ornamenting the lower part of the window, and beautiful deep blue sherds, found near the centre, had no obvious position.

Once the glass was stabilized the leaded pieces, which had distorted slightly due to the fall, could be adjusted to get better and more accurate exterior dimensions which, when clarified and assuming a symetrical design, left a limited interior space into which the remaining pieces could fit. Suddenly the alignment of the loose central piece was obvious and so a considerably larger part of the pattern was established. However the very central area which had distorted when the corner had twisted backwards was still unknown.

The stabilized pieces were transferred to a flat box, which had been lined with a polyethylene foam, known to have no organic decay products (9) (Plate 7). The foam was cut to shape to support each individual piece according to the design so far understood.

It was Sarah Brown of the Royal Commission on Historical Monuments (England) who saw that the central missing portion was triangular in shape and in fact represented a shield. From the pieces of lead remaining it was possible to see that the shield consisted of a chevron and three birds of prey, possibly eagles. Enough transparent glass remained to suggest that the chevron was blue. The birds were held in a red field i.e. the red enamel paint outlining each figure and which continued as flashed red quarries to the edge of the shield. It seemed probably that quarries containing the eagles had been colourless. If so, the bodies and wings, outlined by the red paint, would have appeared 'silvery' against the outside daylight, in heraldic terms representing the 'metal' argent.

Once the whole design was understood it became clear that a border of roundals and flashed red quarries should edge the window, and that these were missing from the top. This was not in fact a complete window but the surviving panel from a larger window, which originally probably footed a second panel incorporating the shield crest.

Plate 7 : Window after conservation, scale 5cm

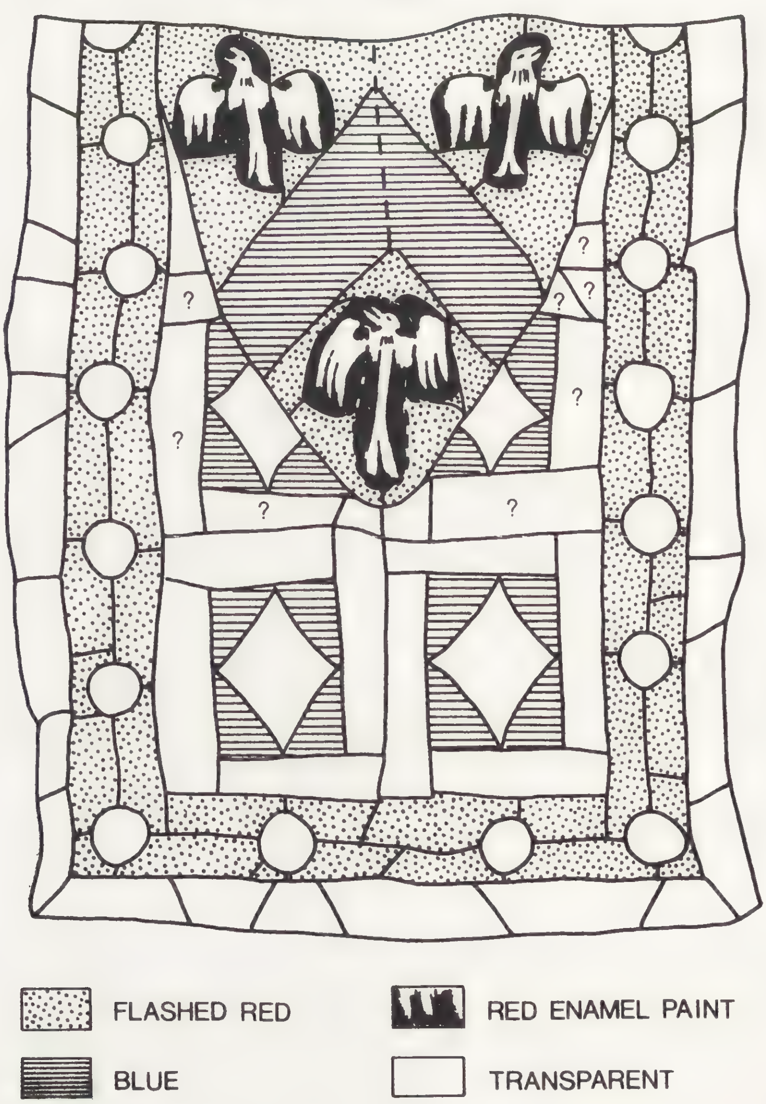


Fig. 2 : Reconstructed window design

The whole panel design is now better understood and a substantial amount of the original colour can be safely estimated. The excavator is at present attempting to identify the person, possibly a benefactor, whose shield was incorporated into this window.

The actual design comprises an outer edge of colourless semi-rectangular quarries, enclosing a double row of flashed red quarries and roundals, colour unknown. The lower portion of the panel incorporates a pair of lozenges outlined in blue glass, and the upper portion contains the shield comprising a probable blue chevron between three birds, silver on red (Fig. 2). Heraldically two colours (tinctures) should not be in contact so it is possible that the chevron is further divided.

The Patron

Several interesting factors have emerged which Sarah Brown noted as pointing to a rich, probably late C13th patron. First the relatively simple geometric design corresponds most closely with late C13th window design. Secondly the fact that the only colours present appear to be red and blue indicates a similar date. Coloured glasses were not manufactured in Britain until rather later (12, 18) so both were expensive foreign imports intended for a high quality window. These could have been brought onto the site in one or two ways, as sheets of crown glass to be cut and worked on site, or just as probably, as whole panels which may have been constructed to order elsewhere and transported to the Friary. However the discovery of four "bull's eyes" (crown glass centres) from elsewhere on site does show that at some point window glass had been worked and fitted at Greyfriars, Carmarthen.

The glass had a flat profile, indicating that each quarry had been cut from the most expensive part of the crown glass away from the "bull's eye", again arguing a wealthy patron. Only one quarry, near a top edge, had the beginnings of a curvature showing it had been cut from close to a "bull's eye". This evidence together with numerous other finds of luxury, foreign goods - e.g. French and Spanish coins, jettons, pottery, and a terracotta statuette decorated with cinnebar, a material only available from Spain in the Middle Ages - paint a picture of an wealthy and colourful establishment.

Display

Ultimately, it is hoped, a replica, based on the evidence acquired during excavation and conservation, will be constructed by students studying stained glass of Swansea College of Technology and the two will be displayed together at Carmarthen Museum, as an example of what can be discovered from an initially fairly unpromising object.

ACKNOWLEDGEMENTS

Many people have helped in this work, in particular I would like to thank Sarah Brown of the Royal Commission on Historical Monuments (England), the excavator Terry James of the Dyfed Archaeological Trust, my colleagues David Leigh and David Watkinson and the people who help lift and treat the window, Dave Crombie, Sue Lloyd-Fern and Diana O'Sullivan

SUPPLIERS

Vinamul 6815	Frank W. Joel Ltd., Unit 5, Oldmedow Road, Hardwick Industrial Estate, King's Lynn, Norfolk, PE30 4HN, Great Britain.
Polyvinyl Acetate	(M.V. about 45,000) BDH Chemicals Ltd., Broom Road, Poole, BH12 4NN, Great Britain.
Paraloid B72 Primal WS-24	Rohm and Haas (UK) Ltd., Lennig House, 2 Mason's Avenue, Croydon, CR9 3NB, Great Britain.
Revacryl 452	Harlow Chemical Co. Ltd., Temple Fields, Harlow, Essex, CM20 2AH, Great Britain
Fibreglass bandage	Scotchcast Casting Products, 2 M United Kingdom PLC, Morley Street, Loughborough, Leicestershire, Great Britain.
Plastazote Polyethylene foam	Wilford Polymers Ltd., Unit 3, Greeves Way Stanbridge, Leighton Buzzard, Beds, LU7 8UB, Great Britain

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the following article the
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a 13th century Syrian ce-
mic dish, where special
ght is thrown on a black
lour pigment used as a
der-glaze-decoration and on
e glaze in question.
e results are compared con-
rrently with a manuscript
om the Middle Ages describ-
g ceramic materials used
a contemporary Persian
tter's workshop (1).
e examinations end up with
reconstruction of the dish.

APPLICATION OF CHROMITE AND ALKALINE GLAZE ON ISLAMIC CERAMIC WARE AND ATTEMPTS OF RECONSTRUCTION

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Introduction

The test material was extracted from the above dish having a porous, yellowish body, black underglaze-decoration and turquoise glaze. The dish belongs to the low fired ceramics - a so-called "Raqqa-ware" - which is often found in archaeological finds, and as a consequence of having been buried for years it is heavily broken down. The decoration of the dish has been done by sgraffito, where the decoration, a tangle of leaves, has been left open in black under the now weathered turquoise glaze. The glaze consists mainly of frail reminiscences and are iridescent in all the colours of the rainbow, which make a deciphering difficult or impossible.

Examination of the black under-glaze pigment

In order to examine the selected material a polished thin section was made at first. Fig. 1 shows the thin section in reflected light and fig. 2 is the thin section of the ceramic ware outlined to clarify the division of layers seen in fig. 1.

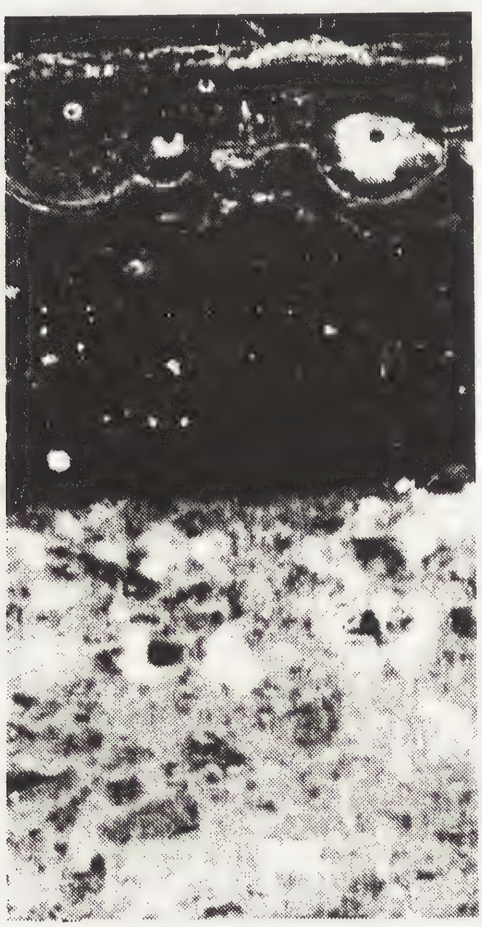

Fig. 1. Thin section.
Reflected light.

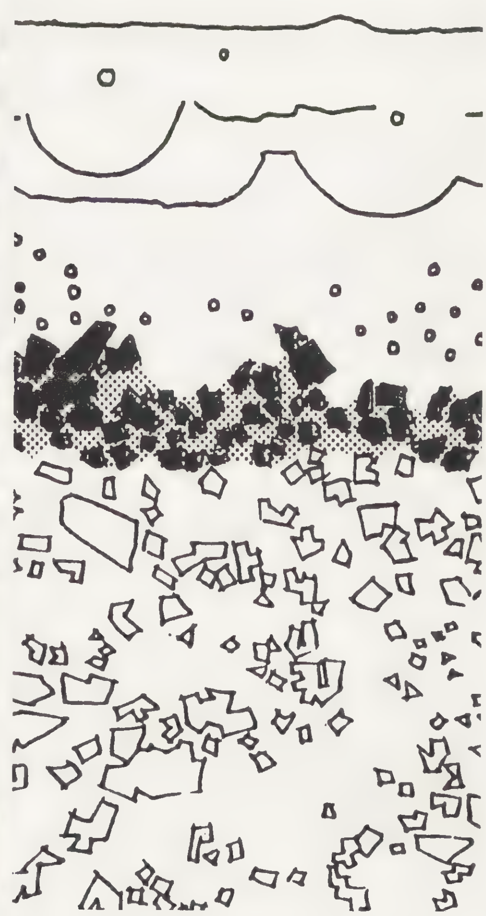

Fig. 2. Outlined thin section.

The building up of the ceramic ware is as follows seen from below and upwards: body, the black under-glaze-decoration in which the sgraffito has been done, glaze and uppermost you can see the weathered glaze as a separate layer of the glaze. When watching the ceramic ware with the black decoration under the turquoise glaze

one might at first presume that this colouring element might be cobalt blue in a concentration high enough to appear black. Possibly, it could also have been a mixed kind, which means that they had mixed various colouring oxides, possibly manganese, cobalt and copper oxide. The following examination showed, however, something else.
The thin section, fig. 1 and the sketch, fig. 2 show that the black mass appears distinctly as a layer between body and glaze. The colour grains are heavily grinded and multibordered as well as completely black, and from the photo fig. 3 it can be seen that these grains are nontransparent.

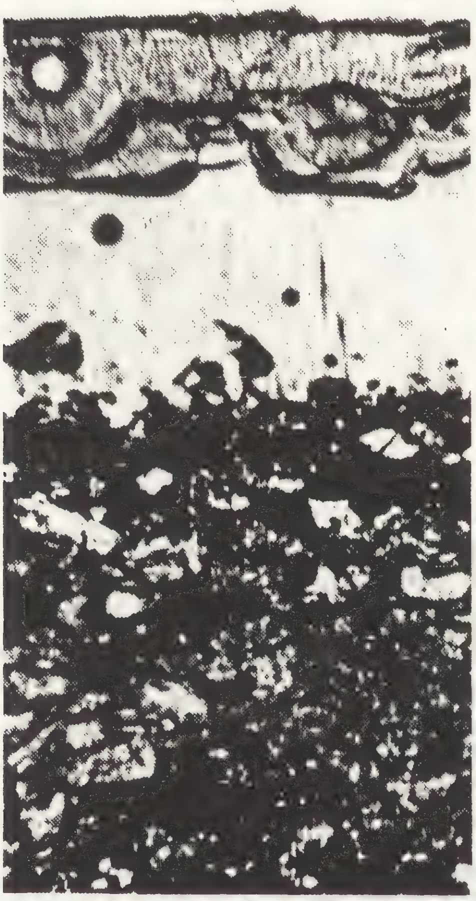

Fig. 3. Thin section. Transmitted light.

Fig. 4. Thin section. Double pol. light.

Furthermore, the thin section shows that this black mass hasn't been melted at the firing of the ceramic ware, as it is seen that the mass still appears as grain. It could be assumed that the ceramic ware was low fired. Partly, because of a non-sintered body and because of the turquoise glaze which is a typical low melting alkaline glaze added copper as colouring element.
If the grains are seen in double polarized light these appear optical isotropic as opposed to the minute optical anisotropic particles that light up among the black grains. The optical anisotropic ones are round sand particles containing silicium which may derive from the body. Fig. 4.
Not until an electron microbeam probe analysis had been carried out was it determined what sort of colour pigment had been used. Before this examination various ores were likely, e.g. magnesiumchromite, $MgCr_2O_4$ or chromite $FeCr_2O_4$.
A cross section of the grains was made for the analysis. This was mounted on a stumplike testholder by means of a piece of double adhesive tape. The cross section was applied with a very thin gold layer to achieve a high picture quality and solvent power.
The method was suitable, as it could analyse the contents of the individual grain. Four different black grains were analysed, and these turned out to have an average content of:

chromium	87%
iron	11%
trace elements (Na, Al, Si, K, Ca, Cu) amounted to	2%

The black layer between body and glaze was identified as chromite, $FeCr_2O_4$ from this analysis.

You can read about chromite that it is a black mineral, that it has a metallic colour luster with brown streak, that the fracture is uneven and that it is infusible and sometimes weakly magnetic. (2). This fitted in well with the information and previous examinations. Furthermore, you can read that chromite is an ordinary component of the socalled serpentinized ignious rocks.
A closer examination of geological maps of Asia showed as well the extension of the serpentine zones, and it appeared that a couple of zones are ranging through all Syria, Mesopotamia and Persia.
In the Persian manuscript from the Middle Ages 700H./1301 A.D. Abulqasim describes the manufacture of ceramic wares in a workshop in Kashan and mentions here some various minerals.
Among other things he mentions a stone, which is "black as coal" and "which comes black glistening out of the fire". This stone is called "Muzzarad", and this could mean very well that here we have the black metallic shining chromite in question. Furthermore, he tells that Muzzarad more often than not is powderized on an oblong grindstone.
What in this connection could seem strange was that the chromite grains were black, and not green to the high content of chrome, but the explanation to this can be that the iron of the chromite simply blurs the green chrome so much that it appears black.

Examination of the turquoise glaze

The glaze is a typical alkaline glaze added copper as colouring element, which is also confirmed by a spectrographic analysis.
By adding such an alkaline glaze to the colour pigment of copper, you could get the characteristic turquoise colour, which is in the glaze of the dish. Contrary to this, copper in a lead glaze would have given a yellow greenish colour.
When observing the glaze in reflected light you notice some blisters in the glaze, and the weathering layer of the glaze appears as a yellowish layer, which has grown unhindered round the blisters in the glaze. See fig. 1.
In double polarized light, fig. 4, you can see the amorphous glaze appears optical isotropic unlike the crystalline glaze weathering which appear optical anisotropic.
Abulqasim relates in the old manuscript how they manufacture glaze by first crushing the materials, then by powderizing these by grinding them on an oblong grindstone and lastly by filtering them.

The glaze was manufactured of 105 parts of filtered "sugarstone", "Hasat", which is quartz, and of 100 parts "Qilj", which is potash. This mixture was put in the oven for about 6 hours, and stirred with an iron spoon until the mass became white.
The potash is more or less concentrated depending what area it comes from, and on account of this more or less potash is used.

By potash, Qilj, is understood potassium carbonate, which is obtained from salt plants "Uşnan", such as Salicórnia and Sálsola, which both belong to the Chenópodiaceae, the ashes of which since days of yore have been used for the manufacture of glass. The potash is a flux, i.e. temperaturelowering for the else high melting quartz.

After eight hours the glass mass is taken out of the oven and is poured into a pit with water in front of the oven. By letting this hot glass mass hit the water it gave a tremendous rumbling sound "as if it were thunder weather", by which the mass was powderized. The workers of the workshop called this powder "Gauhar", i.e. a frit. To this frit, which was the base of the glaze, they had to add lime to achieve a stable glaze, as quartz and potash only give waterglass, which is watersoluble. Furthermore, pigment was added. Owing to the turquoise colour of the glaze on this ceramic dish, you can infer that the dish has been fired oxidizing, since copper oxide or copper carbonate give turquoiseblue under oxidizing oven-atmosphere in an alkaline glaze.

Reconstruction

On making a total reconstruction, you could neither confirm or disprove theories of the manufacture of the dish. Preliminary examinations showed that the chromite for the under-glaze-decoration has been used in a 100% concentration distributed all over the dish in a watery suspension.
To find out the method, clayslips were experimented with added respectively 2,4,6,8,10,40,50 and 80% chromite, which was applied to both "leatherhard" and first firing clay tiles. None of these samples proved to be as good by far.
By mixing the chromite in clayslips, this black pigment was "concealed" in the slipping. Nor did the slipping emerge any clearer on the following glazefiring. From this reason I decided to manu-

facture the above mentioned 100% chromite solution, which gave the right black colour, as the one on the original.
It appears from firing tests that the 100% applied chromite not until after glazefiring has its deep, black colour and becomes intense and sparkling. Without glaze the chromite is rough and brown-black with greyish, metallic body.

What regards the sgraffito, this was done experimentally both on a leatherhard body as well as on first firing body.
At the tests of the leatherhard body it turned out that the chromite very easily spread on the scraped surfaces, and thus "contaminated" these.
When making the sgraffito on first firing body the chromite didn't contaminate the scraped surfaces, since the chromite couldn't find roothold in the hard body, and could therefore be blown away. Besides, the chromite stuck much better on the body after a first firing than on the leatherhard body. After a first firing it didn't stick more, however, than the sgraffito decoration could easily be scraped.

Having this test in mind, it could be assumed that the sgraffito decorations were performed on first fired objects, not leatherhard ones. Another reason for this assumption is that clay objects are less vulnerable to handle in decoration purposes when being first fired, and thus having a strength, as opposed to when they are only leatherhard and are more likely to break. That the sgraffito thus can be performed after a first firing, and not before, appear also if you look at the original dish, where the glaze is on a perfectly clean scrape surface without chromite sediment.

After a number of tests with glazes and firing tests, the best tes with respect to colour and texture turned out to be an alkaline glaze added "Wollastonit", $CaSiO_3$, which means that the strongly alkaline alkaliglaze got its pH changed a bit to the acid side. This was done to change the very cool, blue shade into a warmer blue/greenish one as existed on the original.
Furthermore, tests showed that both chromite and glaze had to be applied in a rather thick layer, as the original's stratification was correspondingly thick.

Thus, the glaze to the reconstruction attempt was made of an alkal frit added 40% Wollastonit, $CaSiO_3$ and 5,5% copperhydroxidecarbonate, $CuCO_3(OH)_2$. Preliminary examinations showed that the kind of clay closest to the original was a so-called "Westwalder'clay", which was added extra lime and quartz, i.e. as much as the clay could absorb without losing its plasticity.
Considering the original it turned out that this had been turned on the potter's wheel. Therefore the reconstruction was turned, to Consideration was taken to shrinkage of the clay, since preliminar examinations had shown that the clay used for the reconstruction had a shrinkage of appr. 10%. This shrinkage was taken into accoun when making the copy, since the copy after drying and firing was to have the same size as the original's. Furthermore, 1% of shrinkage was taken into account for turning off the copy. After turnin the copy/reconstruction had the same measures as the original.

When the copy, then, was leatherhard the chromite was applied in a concentration of 100%, in which the chromite was suspended in wate to a thick, porridge-like substance. Next, the object was dryed at an indoor temperature.
The dish was then first fired at 900°C and was maintained at maximum temperature for 1/2 hour.
After first firing and cooling the sgraffito was performed in the chromite. Then, glazing was done in a thick layer on front side an back side, as it had once been done on the original. Fig. 5.
Glaze firing took place at 980°C (which means a little higher than the theoretical estimate of the original's firing temperature, as the original's firing temperature through Segerformel had been estimated to appr. 925°C), and temperature was maintained for 10 minutes.

If this practical work hadn't been carried out, you couldn't for instance know in what concentration the black chromite had been applied. Nor could you have predicted the troubles of making the sgraffito with the chromite grains contaminating the scrape surfaces. It also appeared from the reconstruction that the chromite's black glaze and depth was a fact owing to the above alkali glaze. Furthermore, it turned out that the chromite could only be used as black colour pigment in compound with glaze. Without glaze the rough brownblack chromite would smudge.

Concurrently, I have made colour pigment examinations of other Islamic ceramic wares, but this work hasn't finished yet. It won't be possible to say whether chromite only has been used as black

colour pigment on Raqqa-wares until all the results are available.

Fig. 5. The sgraffito-decoration on the Islamic ceramic dish.

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Thin section, cross section, microphotos and drawings

Anne-Marie Keblow

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I wish to thank The Geological Central Institute, Copenhagen, where the electron microbeam probe analysis and the spectrographic analysis was done.

SUMMARY

This work reports several years of observations on the desalination of non-metallic artefacts recovered from historic shipwrecks off the Western Australian Coast. The washing of glass, stone and ceramics for periods of up to three years was monitored through regular measurements of wash solution conductivity and chlorinity. Periodic determinations of the concentrations of SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} ions were also made in an attempt to understand the differences in behaviour. Three distinct types of desalination behaviour in static solutions have been observed and the results have been shown to be partly material specific. The diffusion-controlled release rates for removal of chloride ions from glass, stone and ceramics have been determined and the average treatment times are also reported. The results are discussed in terms of the nature of the wreck sites and the length of immersion in sea water.

DESALINATION OF GLASS, STONE AND CERAMICS RECOVERED FROM SHIPWRECK SITES

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Introduction

The problems of salt efflorescence causing loss of surface detail on archaeological materials is well known and a plethora of data exists in reports that describe its nature, composition and cure. Less extensive are the reports that relate primarily to materials recovered from historic shipwrecks and to the problem of desalination of glass, stone and ceramics.[1,2] Since regular monitoring of the treatment solutions has proved to be a useful aid in understanding the stabilization of metallic maritime archaeological objects,[3,4,5,6] it was decided to monitor the desalination of non-metallic materials that included leather, amber, ivory, glass, stone and ceramics. Previous treatments given to wreck material recovered off the Western Australian coast had sometimes resulted in post treatment efflorescence on the surface of salt-glazed stoneware and lead-glazed earthenware objects.[7] The extended washing periods used in this work will hopefully avoid future problems.

Although there are advantages in speeding up desalination through the use of cascade systems,[8] the work reported here relates to static washing primarily because of the problems associated with treating over fifty different sets of objects at the same time and because of curatorial and financial constraints. For example, the supply of reticulated deionized water in the W.A. Museum's conservation laboratories costs approximately $60 per thousand litres.

The artefacts used in this work were recovered from a number of historic shipwrecks off the Western Australian coast, which date from the *Batavia* (1629) through the *Vergulde Draeck* (1656) to colonial period wrecks such as the *Cumberland* (1830) and the locally built *Star* (1880). The glass plate, sheet and bottles that were examined probably vary in composition quite markedly, given that they span a period of nearly four hundred years in their production, and a knowledge of their composition would be of inestimable value in rationalizing apparent differences in behaviour. Elemental analyses for the artefacts are not available and so the data can only be assessed in terms of the nature of the wreck sites and the gross compositional form of the objects. Because of the often turbulent nature of the warm, and well oxygenated wreck sites[9] the extent of material degradation will be more marked than for objects of the same age that are recovered from less hostile locations. A range of glass and ceramic objects were recovered from a relatively sheltered site some 400m from the conservation laboratories in 1983 during a rescue operation. A new marina development for the America's Cup Challenge was to permanently cover part of the site of the old 'Long Jetty' and thousands of bottles dating from the 1850's to the 1920's were recovered from several metres of closely packed sand. Apart from the 'Long Jetty' material, all the other objects have firmly established chronology and provenance which facilitates further studies. Analysis of marine concretions on associated non-ferrous metal objects also provides useful data on the past microenvironment.[10,11]

Experimental

The wash solutions were analysed at intervals that varied from weekly to monthly as the treatments progressed. The containers were made of moulded high density polyethylene with nominal capacities of 20, 40 and 80 litres. The analysis samples were stored in plastic bottles that were shown not to release significant amounts of chloride, sulphate, sodium, potassium, calcium and magnesium ions into deionized water after standing for seven days. Chloride ions were determined coulometrically using a Buchler-Cotlove chloridometer. Sulphate was determined by analysis of excess barium after precipitation and digestion of barium sulphate following the addition of standardized barium chloride. Metal ion concentrations were determined by atomic absorption using standard additives to suppress interference which would otherwise result in variations of up to 20% in the analyses. Objects from the same site were normally separated into collections of like materials in an attempt to see if there were characteristic desalination responses that were material specific. Stabilization of the objects was initially assessed by monitoring the chlorinity of the wash solutions. Since chloride is the most abundant anion in sea water, the overall desalination process would be expected to mimic the removal of chloride. The other advantage of using chloride ions to "monitor the treatment" is that their analysis is much more straightforward than the procedures for sulphate ions. In order to gauge when non-chloride-containing salts were being released, the conductivity of the wash solutions was determined at the same time as samples were taken for chloride analysis. Periodic determinations of the concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} ions were also made.

Results and Discussion

During the course of analysing the data from more than fifty washing experiments some patterns of characteristic behaviour began to emerge. For convenience

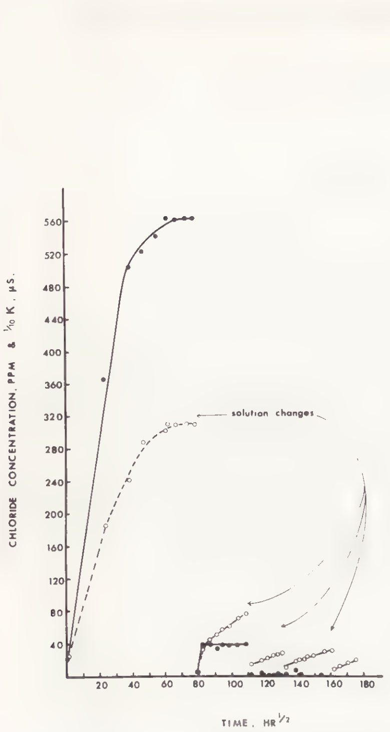


Fig. 1: Plot of chloride ion concentration ● and $^{1}/_{10}$ conductivity ○ against the square root of treatment time ($t^{\frac{1}{2}}$) for desalination of tryworks bricks from the *Lively* (c.1810), in deionized water. The wash volume was 9 litres.

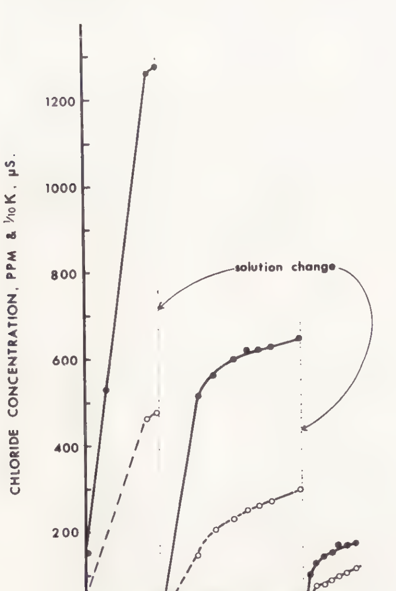


Fig. 2: Plot of chloride ion concentration ● and $^{1}/_{10}$ conductivity ○ against the square root of treatment time ($t^{\frac{1}{2}}$) for desalination of fire bricks from the steamship *Xantho* (1872) in deionized water. The wash volume was 32 litres.

of discussion they are presented in the form of three different responses.

Type 1 - Rapid removal of chloride ions

The mass of data obtained during washing treatments that can last up to thirty months is most conveniently displayed in graphical form with plots of conductivity and chlorinity against some function of time. Most commonly, the data is plotted as a function of the square root of the treatment time since the most frequent "diffusion-controlled" response is that of a linear increase in chloride ion concentration with $t^{\frac{1}{2}}$.[12] After some time the rate of release of chloride ions 'tapers off' until a plateau is reached after which the solution is normally changed and the washing process continues until a second plateau of chlorinity is reached; the procedure is then repeated until the chloride level falls to that of the background deionized water (2±1 ppm chloride).

A typical treatment graph is shown in Figure 1 for the desalination of low fired clay bricks for tryworks from the wreck of the *Lively* (c.1810). After the first change of wash solution the chloride release rate falls to zero, but the conductivity continues to increase as a function of the square root of treatment time ($t^{\frac{1}{2}}$), i.e., the conductivity response is no longer mimicked by the chlorinity data. For conservators who rely on "the silver nitrate test" to ascertain whether or not desalination has been completed, the lack of conducta[nce] data could lead to premature cessation of treatment. The bulk of chloride ions are removed by the end of the second wash but sulphate (and possibly carbonate) salts continue to be released at a steady rate that does not vary significantly with subsequent solution changes. For example the mean rate of increase in conductivity for the last four wash solutions was 8.09±2.8μS.hr$^{-\frac{1}{2}}$.

Analysis of the wash solutions for Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} supports the observation that Cl^- and SO_4^{2-} are the principle anions being released int[o] the wash solutions since the total anionic charge is balanced by the total cationic charge on the assumption that the above-mentioned ions account for 95-98% of the soluble species. A total of eighteen different desalination treatments showed very similar characteristics to that displayed by the trywor[ks] bricks from the *Lively*. During the first wash, the mean value of the ratio of sodium to potassium (expressed as ppm) was 21.7±5.4 which is essentially the same as that for 'normal' sea water which has a value of 28.3.[13] For the third and fourth washes the $^{Na}/K$ ratios were much lower with typical values ranging from 4.8 down to 1.2 . We do not believe that hydrolysis of glass is a major source of sodium and potassium ions in the wash solutions since simila[r] concentrations and ratios were found in treatment solutions that covered a wid[e] range of materials from sandstone, bricks, stoneware, bone china and earthenwa[re] to glass. It is essential that analysis of the surface characteristics of the wreck materials at all stages of the desalination process be undertaken in the future since it is only through such work that details of the mechanisms controlling release of salts can be elucidated.

For objects that conform to the type 1 behaviour (see Figure 1) the ratios of the concentrations (ppm) of calcium to magnesium found in the early and late stages of the desalination process are apparently sensitive to the type of material. For porous materials such as sandstone water purifiers from the *Cumberland* (1830) the $^{Ca}/Mg$ ratio does not change significantly during the course of desalination and remains at 3.7±1.0 . The mean value of the $^{Ca}/Mg$ ratio for desalination of earthenware is much the same as that found for stone viz., 3.2±1.8 whereas the situation with glass objects is markedly different. During the early stages of glass desalination the $^{Ca}/Mg$ ratio is 13.2±1.5 whil[e] in the later washes, when the bulk of the chloride ions have been leached out, the ratio falls to a mean value of 6.3±1.1 . The differences in behaviour probably lie in ion-exchange processes at the corroded glass-wash solution interface.[14]

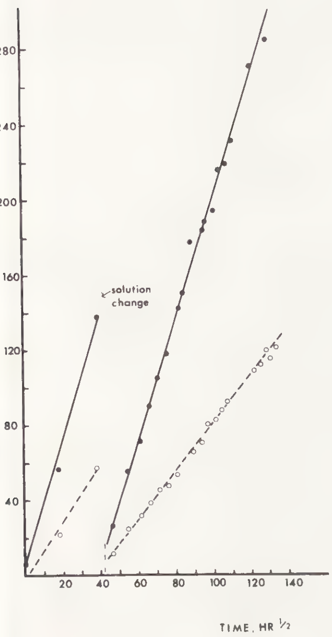
Type 2 - 'Slow' removal of chloride

The desalination of some fire bricks from the engine room of the SS *Xantho* (18[72]) is an example of the second type of desalination response. A plot of the data obtained during the first twenty-one months of treatment is shown in Figure 2, where the chloride ions are seen to report to solution at roughly the same rat[e] during the initial stages of each wash until the rate becomes much slower as a plateau is approached. Solution changes were made prior to the establishment of a more definite plateau since it was readily apparent that the rate at whic[h] the salts were dissolving was diminishing. The conductivity data mimics that of the chlorinity profile (or vice versa) for the three stages of the treatmen[t]. This behaviour may be contrasted with that shown in type 1 where there appeare[d] to be a more rapid removal of chloride ions than sulphate ions. Effects such [as] ion pairing of sulphate and magnesium/calcium ions in the cracks and micro-fissures of type 1 materials could account for the differences in behaviour. The ratios of $^{Na}/K$ and $^{Ca}/Mg$ found at various stages of desalination for glass and stone/fire bricks objects that showed type 2 behaviour were not significan[tly] different from those found for type 1.

Type 3 - Steady removal of chloride

A third type of response was shown by two sets of glass bottles from the site [of] the Long Jetty, some 50m from the shoreline of Bathers Bay, Fremantle. A plot

of the conductivity and chlorinity data is shown in Figure 3, where it can be seen that the sea water salts are still coming out at the same rate as they were some 700 days prior to the time of writing this report! Apart from an inadvertent solution change at 74 days (42.14 $hr^{\frac{1}{2}}$) when the objects were needed for a media release, the chloride ions are still being released at the rate of 33 $ppm.hr^{-\frac{1}{2}}$ or $37\mu g.cm^{-2}.hr^{-\frac{1}{2}}$ after the data has been corrected for the solution volume of 50 litres and an apparent geometric surface area of $44{,}100 cm^2$.



g. 3: Plot of chloride ion ncentration ● and $^1/_{10}$ conducti- ty ○ against the square root of eatment time ($t^{\frac{1}{2}}$) for desalina- on of glass bottles from the ng Jetty site, in deionzed ter. The wash volume was 50 tres.

Prediction of treatment times and release rates

A question of major importance to those concerned with managing a conservation facility or running an excavation is, how long will the desalination process take? There are advantages in the allocation of resources if one could simply look up a table of treatment times for different types of materials and begin to desalinate without having to devote time to proper monitoring. The first two types of desalination behaviour release characteristic amounts of chloride at each stage of the treatment and these are summarised in table I. For type 1 materials it may be sufficient to use only two washes since this would remove roughly 98±7% of the available chloride whereas a similar approach for type 2 materials would only remove 86±8% of the chloride.

One important variable in the desalination process is the time it takes to reach the first and subsequent plateaus, since it is only after the chloride release rate falls to zero that the solution needs to be changed. The mean values of the time taken to reach the first and second plateaus for both type 1 and type 2 are listed in table I. Although type 1 takes an average of twenty more days to reach its first plateau than type 2, the difference is not significant because of the large scatter in the data. Similar comments about the large variations in the mean values can be made for the data relating to the times taken to attain the second plateau. As far as chloride removal is concerned, the type 1 objects will be 'stabilized' in approximately one third the time taken for type 2. Although chloride removal is a major consideration in the stabilization of the wreck material the problems associated with insufficient removal of soluble sulphates are well known[15], since cycling of relative humidity will cause stress in the object as the chemical composition of the residual salts changes.

In an attempt to rationalize the observed chloride release rates, the raw data was 'normalized' to correct for surface area and solution volume according to the formula R_N = Rppm x/y where x is the wash volume in litres and y is the geometric surface area in square centimetres. With such a wide range of materials being examined, there is only a remote chance that any systematic trends will be observed since the real surface area of the objects could easily be an order of magnitude greater than the geometric value. When all the data is collated without regard to the physical nature of the object there are no discernable differences in chloride release rates. However, when materials are grouped some general trends emerge (see table II). The differences in the mean values of the rates for chloride removal from glass, stone, fire bricks and clay bricks are not statistically significant. However, the differences are significant for the earthenware group.

One of the main driving forces associated with the outward diffusion of salts will be the concentration gradient across the boundary between the object and the wash solution.[16] The mean values of the total amount of chloride removed during desalination can be conveniently expressed as the wt% chloride, and as such can be used as a measure of the driving force in the desalination process. For type 2 earthenware the mean chloride content was 0.17±0.05 wt% while for type 1 the value was 0.10±0.08 wt% (see table III). Whilst it is realised that total salt content will be only one of the parameters controlling the overall rate of desalination, the above does provide a ready rationalization of the observed differences. By way of comparison there is roughly the same amount of chloride released from stone and bricks as with earthenware and glass recovered from aerobic sites. The somewhat lower value of chlorides found in glass from anaerobic sites may be a reflection of the fact that the extent of 'corrosion' will be less for materials that are not being subjected to fully oxygenated conditions and strong surge (see table III).[17]

Various proposals have been made concerning the use of 'corrosion layers' on glass as a means of dating.[18] It was therefore of interest to look at the amount of chloride in the objects as a function of the years of immersion. The results show a remarkably uniform set in that the mean values of chloride (ppm per year of immersion) are the same for anaerobic and aerobic glass as for stone and bricks. The major difference occurs for ceramics and this is probably due to their composition.

The removal of soluble sulphates is less well documented because of the analytical procedures involved in the quantitative determination of sulphate ions. However, once the chloride ions have stopped reporting to solution the conductivity will be mainly due to sulphates. For type 1 materials, the conductivity increases at a steady rate for the third and fourth washes regardless of the solution being changed (see Figure 1). The conductivity data can be rationalized using the same type of procedure as outlined for normalizing the chloride release data. For type 1 glass the normalized 'sulphate' release rates are $8.4\pm5.9\mu S.cm.hr^{-\frac{1}{2}}$ while for sandstone, bricks, etc., the rate is

$48 \pm 16 \mu S.cm.hr^{-\frac{1}{2}}$. Washings are not continued beyond 40 months as the amount of soluble salts reporting to solution is very small and the risk of damage to the object by prolonged immersion in deionized water is greatly increased.

Conclusion

The monitoring during extended washing of glass, ceramic and stone artefacts from shipwreck sites has shown that the release of salts is diffusion controll Analysis of the conductivity and chlorinity data has shown that there are three types of responses and that it is now possible to predict the extent of removal of chloride ions at each stage of the desalination process. The chloride rele rates have been rationalized in terms of the nature of the materials and their porosity. The total amounts of chloride removed from glass, ceramics and stone are very similar and the results indicate that a major factor in the incorporation of salts is the length of immersion in the sea.

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Table I: Kinetic parameters for the desalination of glass, stone and ceramic objects recovered from shipwreck sites.

	Type 1	Type 2
% chloride extracted 1st wash	90.4±4.7	49.8±5.1
% chloride extracted 2nd wash	8.1±3.8	36.5±3.2
% chloride extracted 3rd wash	1.9±1.6	15.1±2.2
Time to reach first plateau (days)	64±28	44±10
Time to reach second plateau (days)	138±51	229±95
Time to reach third plateau (days)	n.a.	268±175

Table II: Normalized chloride release rates for desalination of glass, stone and earthenware in deionized water.

	Type 1	Type 2
Glass*	3.7±1.2	9.5±6.5
Stone, bricks*	97±58	78±13
Earthenware*	2.3±1.8	24±10

*The units for the release rates are $\mu g.cm^{-2}.hr^{-1/2}$

Table III: Chloride extraction characteristics for desalination of shipwreck materials.

	Wt% Cl^- extracted	Cl^- extracted per year of immersion as ppm of object wt.
Glass - aerobic	0.12±0.06	10.0±5.9
Glass - anaerobic	0.06±0.02	9.4±5.4
Stone	0.12±0.07	8.9±4.8
Ceramics	0.12±0.08	3.5±2.7

UMMARY

ledieval stained glass decays mainly ırough the attack by water (as rain ı the outside of the window or as ondensation on the inside). ttempts have therefore been made prevent or reduce this attack om water by using a 'protective' ating of a resin. At one time it as believed that the resin coating ight cause more damage than it evented because the alkaline oducts of the attack would be apped between the glass and the sin. The author explores the idence and concludes that the otective effect may be better than any investigators had feared.

WHAT DO WE REALLY KNOW ABOUT 'PROTECTIVE COATINGS'?

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It has been known for a long time that water is the principal agent which causes the deterioration of glass [1]. Medieval stained glass is particularly susceptible to attack by water because it is a potash glass with too much lime to have a good durability [2]. In the early 1970s, various synthetic resins were advocated by their manufacturers as being 'impervious' to water and consequently useful both for preparing appliqué windows (in which coloured glass was to be stuck to a support glass to make decorative panels [3]) and for coating important stained glass to protect it against harmful agents in the environment [4, 5, 6].

Many conservators hoped that these resins would have a revolutionary effect on the conservation of medieval stained glass, by providing both repairing agents (fillers) and coatings which would completely protect the glass against the known harmful effects of water or water vapour (or of other noxious pollutants which need water to assist any adverse effect which they may have on poorly durable glass). Two well known instances of the use of coatings of Viacryl VC-363 were on (a) a special test panel of medieval glass in December, 1971, at the church of St. Maria am Gestade in Vienna [4], and (b) the Jesse Tree window of the west front of Chartres Cathedral [6].

At that time considerable doubts were raised about the consequences of using resin coatings on poorly durable glass [5]. The doubters then believed that several things would happen; (a) water would probably diffuse through the coating (or water vapour would certainly do so) and reach the surface of the glass. (b) The molecules of water at that surface would then undergo ion exchange with the cations in the glass to produce alkali hydroxides in the (film of) water. (c) Being 'trapped' between the resin coating and the glass, the aqueous film would become progressively more alkaline until, when its pH value reached a value of about 9.0, the silicate network would be attacked and the glass would be seriously damaged. Such warnings seem first to have been advanced as early as 1953 by Schröder [7], although Moore had made a similar pronouncement at a slightly earlier date (about 1950), but his remarks were not published until some twenty years later, and eleven years after his death [8]. In 1958, Werner (apparently independently) provided a carefully reasoned account of all the problems [9], and he repeated them eight years later [10].

In the meantime, glass-reinforced plastics (GRP materials, glass-fibre car bodies, glass reinforced drain pipes, etc) were encountering premature failures due to the loss of mechanical strength from attack by water on the glass at its interface with the resin. In order to combat this problem, various 'coupling agents' were advocated [e.g., 11, 12]. They were intended to (a) improve the bond between the resin and the glass and (b) produce a water-repellent (hydrophobic) surface. A four-fold improvement was achieved and, as a twenty year life was all that was then required from GRP materials, the result was regarded as satisfactory. Such a short protective period would be of no use for cathedral windows, although a twenty-five year life was considered satisfactory for the reconstructed Churchill Memorial Window in the Dudley shopping precinct [13]. Nevertheless, that window seemed to be showing signs of failure in 1986, only about 14 years later. One scientific article even suggested, on thermodynamic grounds, that resin coatings may never be able to protect glass completely against attack by water vapour [14].

Somewhat later, a hitherto unsuspected additional problem was brought to light concerning the 'protection' of church windows by resin coatings. If a resin is used at temperatures above its 'glass transition temperature' (Tg), particles of dust which settle on its surface can migrate into the interior, making the resin appear 'dirty' and less transparent [15]. The resin Viacryl VC 363 has a Tg value of +15°C, and thus, especially on a south-facing window, it will be warmer than its Tg value for much of the year. This seems to have been happening, after 14 years, to the Dudley Churchill window and, in addition, micropitting of the surface seems to have taken place there, so that dirt can enter the pores. Although this may not matter much in the case of an appliqué window, it could have an adverse effect on the appearance of a 'resin-protected' stained glass window. As recently as 1984, however, there were still fears that a 'protective coating [could] accelerate the corrosion of glass instead of stopping it', see page 11 of [16]. Between 1973 and 1976, strenuous efforts had been made to organize concerted research into the whole problem, under the aegis of the

European Science Foundation, but it came to nothing [17]. Other efforts to undertake a serious study, but which came to nothing, have been summarized in [18].

Despite all these misgivings, a fundamental research programme was started (in about 1982) at the Fraunhofer Institute for Silicate Research at Würzburg, under the then Director, Professor Horst Scholze [19]. He continued, with support from the NATO CCMS programme, to make an intense study of the properties of special resins, and of silane hydrophobic treatments of the glass. This is probably the most comprehensive study yet undertaken for synthesising special resins, and treatment systems, for coating glass. It was concluded that special bifunctional resins could be prepared which would be expected to form chemical bonds with the glass surface (via their silane groups), and also repel water from the resin surface (via their aliphatic or aromatic groups. These new resins were called "ORMOSILS" (ORganically MOdified SILicates) and, in 1984, several promising ones had already been tested as coatings for glass. They all caused a substantial delay in the rate at which water would attack the surface (as shown by an increase in the hydoxyl groups found by infra red spectroscopy), but none of them entirely stopped the attack. Water was able to reach the interface between the resin and the glass, produce an alkaline layer, and cause attack on the glass [20].

At that time, and until only very recently, it was believed that this 'alkaline film' would cause the attack to proceed from bad to worse until, perhaps, the glass could be destroyed in its entirety. For this reason, in about 1985, the emphasis of the work at Würzburg changed and they tried to delay the attack even further by adding flaky material (glass flakes or fine mica particles) to their best resin coating so that the diffusion path would be made much more difficult, and hence delay the ingress of water even further. The result has been successful and there has been a thirty-fold delay in the onset of the attack [20].

In the meantime, in 1977, the Austrian workers who had coated the test panel at St. Maria am Gestade [4] wished to learn what had happened to the glass beneath their coating of Viacryl. They removed the resin (by swelling it in 'Cital 12/12' so that it was soft enough to come away with gentle rubbing) and discovered that the attack on the glass was much less than had been feared [21]. The French workers have not yet (late 1986) tried to remove any of the Viacryl resin from the west front at Chartres, so we do not yet know what has been taking place under the resin there.

The Austrian discovery, that little damage has occurred in the Viennese experiment, requires some explanation, and yet another feature has recently come to light. Some American workers, who were primarily concerned with the encapsulation of high level radioactive nuclear waste in glass [22], had tried to simulate what might happen if a very small crack had formed in the container for the encapsulated waste, and 10,000 years might have passed! In other words, instead of starting with pure water (as other workers had done), they assumed that a minute amount of water had reached the glass, and that enough time had elapsed for the water to have become *saturated* with reaction products from the glass. They discovered that their saturated solution failed to attack the glass, even though the pH value was higher than 9.

To extend these American results to the case of a resin coating, the suggestion would be that the water, which is expected to reach the interface between the resin and the glass, would attack the glass and eventually saturate the 'water film' with reaction products. The saturated film might then cease further attack on the glass, and this surprising conclusion may explain what seems to have occurred in Vienna (and may also have occurred at Chartres, if anyone is prepared to try to find out).

Some experiments have therefore been started at the University of Sheffield, using poorly durable model glasses and leachant solutions prepared by shaking powdered glass (of the same composition) in distilled water for long periods of time. The saturated leachant being prepared rapidly reached pH=9 (in less than an hour) and, when a piece of the model glass was immersed in it, very little attack was produced on the surface, as shown by the infra red spectra, compared with the large changes produced when repeatedly renewed distilled water had been used as the leachant [23].

The experiments will take a long time to complete, and this report must therefore be only a preliminary one. There will also be many other questions to be answered, such as:- would not more water be expected to reach the interface by the original route and dilute the water film? Would not osmotic effects produced by the saturated solution force even more water through the resin film than had occurred before, and thus dilute the solution even more, so that attack on the glass would be resumed?

It need not be surprising that this 'saturation effect' had not been reported by the earlier workers who used resin coatings under experimental conditions, such as those

who carried out the careful experiments at Würzburg [20]. Most of these experimenters stopped their tests when some attack on the glass had been demonstrated, because it had been believed that 'the resin had failed' and there was therefore little further interest in that experiment. It is thus possible that, had these tests been continued (as had been the case with the outdoor exposure for five years in Vienna), the rate of attack might have decreased and eventually come to a stop. The author hopes that this preliminary report will encourage the kind of discussion of the whole question which should have been taking place long ago, certainly as early as 1976 when the ESF was ready to work on the problem if the committee members had really wanted to suport it.

The concepts in this paper were first put forward at a Symposium "Klosterkirche Königsfelden" organized by the Baudepartment des Kantons Aargau, Switzerland, on 26-27 June, 1986.

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ABSTRACT

Glass artefacts recovered from the wreck of the "Mary Rose" presented problems in drying and consolidation. A series of experiments were undertaken to establish a successful treatment system that was then applied to the Tudor artefacts.

AN INVESTIGATION INTO THE DRYING AND CONSOLIDATION OF WET GLASS RECOVERED FROM THE "MARY ROSE"

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Introduction

In 1545, the "Mary Rose", once the Flagship of Henry VIII, sank in the Solent off Portsmouth during an action with the French. The site of the wreck was not rediscovered until 1965 when project "Solent Ships" was set up to investigate historic wrecks in the area. The Mary Rose Trust was formed in 1979 with the aim of excavating and raising the ship so that she could be placed in a purpose-built Ship Hall and Museum. Many artefacts of wood, leather, metal and glass were recovered, all requiring urgent conservation. This paper deals with one type of material, glass, and the problems associated with it, and methods used for drying and consolidation.

The Problem

The weathering crust so often seen on glass recovered from a marine site is very fragile and easily removed from the glass body. Once removed, the bare glass surface revealed is susceptible to further attack. The crust may well act as a barrier to further deterioration and should be left in situ. The conservator's aim is to find a suitable means of drying out the glass without causing further damage to the material, and applying an adequate consolidant that will bind the weathering crust to the glass beneath.

Experimental Work

Due to the intrinsic value of the few Tudor glass artefacts recovered from the site, all experimental work was undertaken on pieces of post-Tudor glass recovered from the upper layers of the wreck. These items consisted mainly of bottle fragments in varying states of deterioration.

The experimental work was divided into two categories - aspects of drying and suitable consolidants.

Drying Techniques

Two methods were looked at. These were air drying and solvent drying. Air drying was carried out under normal room conditions, the ambient temperature 20°C and an average RH of 50%.

Solvent drying involved acetone and industrial methylated spirits (I.M.S.), both common in conservation. A four bath process was used with each solvent, each bath containing a solvent/water mixture. The concentration of solvent used in the baths was 25%, 50%, 75% and finally 100%. Each sample was immersed in each bath for four hours.

Once through the bath process, the solvent was then allowed to evaporate in one of two ways:

a. Rapid evaporation at room temperature.

b. Slow evaporation in a solvent-saturated atmosphere.
The solvent-saturated atmosphere was achieved using a glass desiccator filled with the correct solvent. The sample was then placed in the desiccator for two days, after which it was taken out into the room atmosphere.

Consolidation

Once dry, the glass samples were coated with various consolidants to test their efficiency at binding the crust to the glass.

The consolidants tested were:-

Paraloid B72. A methyl acrylate/ethyl methacrylate copolymer soluble in toluene, xylene, acetone and trichloroethylene.

Silane T40149. A trimethoxymethyl silicone monomer, polymerised by the addition of 1% catalyst. Commonly used as a stone consolidant.

Vinamul 6815. A polyvinyl acetate emulsion, which is a water soluble.

Elvacite 2013. A methyl/n-butyl methacrylate resin soluble in xylene, tolvene and acetone.

These consolidants have low enough viscosities to be able to penetrate weathering crusts, thus adhering them to the glass below.

Apart from Silane, a 5% solution was used, Vinamul in water, and Paraloid B72 and Elvacite 2013 in toluene.

Preliminary work had revealed that once glass had been dried, the weathering crust was very fragile. Upon immersion in a consolidant, parts of the crust would flake off the object. Therefore, it was impossible to apply the consolidant by immersion techniques. Instead, a pipette or thin, soft brush was used.

Each consolidant (apart from Vinamul 6815) was tried on glass having been dried previously by one of the stated methods. In the case of Vinamul, which is water soluble, wet glass was immersed in the consolidant and left for five days. The glass was then removed and allowed to air dry over a period of two weeks before being examined.

<u>Results</u>

<u>Drying</u>

The results are shown in Table 1.

TABLE 1 EFFECTS OF DRYING

METHOD	SURFACE ALTERATION	COMMENTS
Air drying	yes	Process is slow - on average two weeks-crust easily falls off during drying.
Acetone, Fast evaporation	yes	One day for solvent to evaporate. Crust fragile.
Acetone, Slow evaporation	yes	Five days in desiccator. After removal, crust is fragile.
I.M.S, Fast evaporation	yes	One day for solvent to evaporate. Crust fragile.
I.M.S, Slow evaporation	yes	Five days in desiccator. Crust fragile.

The results show that for drying, there appears to be little difference between the use of either acetone or I.M.S. Also, there is very little difference in the results from either slow or rapid evaporation of the solvent.

During the air drying process, it was found that crust or deterioration layers had a tendency to spall off the glass.

<u>Consolidation</u>

The results are shown in Table 2.

TABLE 2 EFFECTS OF CONSOLIDANTS TESTED

CONSOLIDANT	AVERAGE NO. OF APPLICATIONS	BOND OF CRUST/GLASS	COMMENTS
5% Paraloid B72	5	Good	No alteration of appearance of surface.
Silane T40149	1	Good	Sometimes glossy appearance.
5% Elvacite 2013	7	Fair	No alteration of surface appearance.
5% Vinamul 6815	Bath immersion of wet glass	Fair	Excess Vinamul on surface often a problem.

From the results, both Paraloid B72 and Silane T40149 successfully bonded the crust to the glass surface.

During the use of Vinamul, if the consolidant was not cleaned off the glass surface before drying, a glossy sheen on the glass often resulted. On average, more coats of Elvacite 2013 were needed.

Conclusions

Although the work was carried out on post-Tudor samples, the nature of the deterioration was similar to that of the Tudor glass and so the results of the experiments can be applied to both cases.

Solvent drying is recommended over air drying because of the time involved. In addition, the longer time needed to air dry brings a greater risk of the weathering crust being damaged and flaking off the glass.

Very little difference could be detected between the use of either solvent, or between rapid and slow evaporation of the solvent.

Both Paraloid B72 and Silane T40149 produced favourable results, but due to the irreversibility of the Silane, the use of Paraloid B72 is to be recommended.

Following on from this, the Tudor glass artefacts were treated in the following method:-

1. Dehydration using I.M.S. Four baths of 25% solvent/water, 50% solvent, 75% and 100% solvent. Glass in each bath for four hours.

2. Slow evaporation of solvent in a solvent saturated atmosphere for two days.

3. Consolidation of crust using 5% Paraloid B72/toluene, applied with a brush.

Post Conservation

Once treated, the Tudor glass was stored in the Trust's Inorganic Store at an RH of around 45%. The pieces were constantly monitored for further signs of deterioration.

After a couple of years, it was observed that several of the pieces were active - spalling of the weathering crust was occurring.

These pieces were re-submitted for further consolidation with 5% Paraloid B72 then re-stored in the Organic Store where the relative humidity was at 55%. The glass artifacts were placed in the Organic Store at the beginning of 1986 but it is still too early to judge if they are more stable in this new environment.

Suppliers of Materials

Acetone	)	Frank Joel Ltd.
Industrial Methylated Spirits	)	Unit 5,
Paraloid B72	)	Old Meadow Road
Elvacite 2013	)	Harkwicke Indust. Estate,
Vinamul 6815	)	Kings Lynn, Norfolk
		PE30 4HN, England

Silane T4014a is now no longer available from Frank Joel Ltd.

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A COMPARATIVE STUDY OF SOLUBLE SALTS IN CONTAMINATED CERAMICS

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SUMMARY

A comparative study using sodium chloride solutions of concentrations from 1 to 1000 ppm (mg/l) demonstrates the conversion of quantitative expressions for the testing of soluble salts in ceramics. A comparison is made between the chloride titration precipitate, concentration in solution as ppm (mg/l), µsiemens/cm (µmhos/cm) of conductivity, and a percentage as wt/vol in solution. The applicability of the conversion of these units of measurement to monitoring the removal of soluble salts from ceramics is illustrated. The need for the compilation of conversion charts for the various soluble salt compounds found as contaminants in ceramics is expressed.

INTRODUCTION

The removal of soluble salts from contaminated ceramics is often necessary to halt deterioration in progress and to prevent the possibility of further damage by the soluble salts. Quantitative testing is required to determine the extent of contamination, to monitor the removal of soluble salts and to establish the completion of the extraction process. There are several methods available for measuring soluble salts during their removal by immersion in water (Paterakis,1987). Depending on which method is used, the quantitative expression of the soluble salts in solution may be ppm (parts per million) as mg/l or moles/moles, µsiemens/cm or µmhos/cm, a percentage % of soluble salts as wt/vol or wt/wt, or the opacity of the silver chloride precipitate in the silver nitrate test (Plenderleith,1976,p.201). Acceptable concentrations of soluble salts in the final extraction solution have been given as 150 µsiemens/cm or less for all dissolved salts (Olive & Pearson,1975,p.65) and between 75 and 100 µsiemens/cm for chlorides by the author (Paterakis,1987). If the published µsiemens/cm figures are used as an indication of the completion of of the extraction process, test units of measurement must be converted accordingly.

COMPARATIVE STUDY

A comparative study is presented to illustrate the importance of the conversion of units of measurement for the removal of soluble salts from ceramics. A contribution toward the conversion of the expression of measurement for soluble salt concentration was made by Semczak in his comparison of the opacity of the silver chloride precipitate with the chloride ppm concentration of the test solution (Semczak,1977,p.41). In the present study the comparison between the opacity of the silver chloride precipitate and the chloride ppm concentration is extended to include µsiemens/cm of conductivity and a percentage % of soluble salts in solution. In this comparative study chloride solutions were prepared in concentrations of 1,5,10,20,30,40,50,100,200,300,400,500,600,700,800,900 and 1000 ppm (mg/l) of chloride.[1] The NaCl was weighed at room

Figure 1 silver chloride precipitates
Cl ppm concentration from left to right 1,5,10,20,30,40,50, & 100

temperature for each of the solutions using a scale with a precision factor of .0001 and dissolved in distilled water. These solutions were given the silver nitrate test, the precipitate stirred, then photographed after ten minutes as in the work by Semczak (Semczak,1977,p.41) (Figure 1). The solutions from 200 to 1000 ppm did not display sufficient differentiation in opacity to be used for comparison and therefore were not photographed.

The concentrations in ppm as mg/l were derived from the atomic weight of the NaCl compound rather than of the chloride only so that the conductivity of the salt compound is considered rather than of the chloride alone. The chloride concentrations in ppm of the solutions in Semczak's work were determined with a specific ion electrode for chloride (Semczak,1977,p.40).[2] This electrode does not measure the concentration of the mineral ion of the chloride compound, for example potassium or sodium. The mineral ions, potassium, sodium, magnesium, etc., contribute to the conductivity of the salt compound in solution which causes some variation in the conductivities among the various salt compounds such as NaCl, KCl, and MgCl.

Since the majority of conservators will most likely have access to a total ion conductivity meter rather than a specific ion meter and electrodes, it was considered best to use a total ion meter to monitor the conductivities in µsiemens/cm of solutions with known ppm (mg/l) concentrations. The meter was first calibrated using a standard KCl solution. A Ciolfi conductivity meter, model CC BR, for total ion concentration was used to measure the solutions at a temperature of 22°C.[3]

INTERPRETATION OF RESULTS

The opacities of the silver chloride precipitates in the photograph of this study (Figure 1) may be used for visual evaluation of chloride concentration. For those who have only the silver nitrate test at their disposal to determine chloride concentration an approximation of the concentration up to 100 ppm (mg/l) may be derived by visual comparison with this photograph (Figure 1). Beyond this concentration the silver nitrate test is solely a qualitative indicator of chlorides. The approximate conductivity of the chloride ions in solution may then be found from the chloride ppm figure in Table 1. For test solutions which contain more than 100 ppm chloride means other than the silver nitrate test are necessary for a quantitative determination expressed as ppm of concentration or µsiemens/cm of conductivity. If a conductivity meter which measures all ions in solution is used for monitoring the salt extraction of ceramics, it is useful to compare the µsiemens/cm reading with the opacity of the silver chloride test precipitate to determine to what extent chlorides may account for the conductivity reading.

TABLE 1
Results of Comparative Study

solution #	Cl% wgt/vol	Cl ppm mg/l	NaCl ppm mg/l	µmhos/cm 22°C	empirical factor *
1	.1	1	1.648	18	.0915
2	.5	5	8.24	27	.305
3	1	10	16.48	47	.350
4	2	20	32.96	74	.445
5	3	30	49.44	95	.520
6	4	40	65.92	130	.507
7	5	50	82.4	160	.515
8	10	100	164.8	300	.549
9	20	200	329.6	560	.56
10	30	300	494.4	850	.58
11	40	400	659.2	1200	.549
12	50	500	824	1400	.66
13	60	600	985.8	1700	.581
14	70	700	1153.6	1900	.607
15	80	800	1318.4	2200	.599
16	90	900	1483.2	2400	.618
17	100	1000	1648	2700	.610

* derived from NaCl ppm and µmhos/cm figures

Table 1

Table 1 compares the various units of measurement for soluble salts in solution using the sodium chloride solutions of this comparative study. If an approximate chloride concentration of 20 ppm is ascertained by visual evaluation of the AgCl precipitate opacities, a look at Table 1 shows that the percentage % of chloride is 2% and the conductivity at 22°C is approximately 74 µsiemens/cm for sodium chloride. If the figure 75-100 µsiemens/cm is chosen as an indication of the maximum acceptable concentration of chlorides during the extraction process, one may stop washing when the opacity of the AgCl precipitate most closely resembles that of test solution #4 in Table 1 (Paterakis,1987).

TABLE 2
Conductivities of KCl Solutions *

Cl ppm mg/l **	KCl ppm mg/l **	µmhos/cm 25°C	empirical factor ***
3.547	7.45	14.94	.49
17.717	37.25	73.90	.50
35.43	74.5	147	.506
177.17	372.5	717.8	.518
354.34	745	1413	.527
705.68	1490	2767	.538
1771.7	3725	6668	.558

* from APHA,1975,pg.73
** derived by the author
*** derived by the author from KCl ppm and µmhos/cm figures

Table 2

If the chloride concentration in ppm of the test solution has been determined but the mineral ion forming the compound has not been identified, the conductivity figures for sodium chloride in Table 1 may be used only as a very approximate indication of conductivity. Since chloride represents different percentages of each salt compound (e.g. 60.66% of NaCl and 47.55% of KCl) it is best to use the ppm concentrations of the salt compound for evaluation and comparison of conductivities rather than the ppm concentration of the chloride alone. If the chloride concentration in ppm of the test solution and the mineral ion forming the compound are known, the ppm concentration of the compound may be determined from the molecular weight of the compound. A comparison of conductivities of NaCl and KCl solutions based on concentration in ppm of their compounds are relatively close in value in Table 1 and Table 2. With an increase in soluble salt concentration the conductivities of solutions of the two salt compounds of the same concentration coincide (Table 3).

TABLE 3
Conductivities of NaCl and KCl Solutions*

salt	compound ppm mg/l	Cl ppm mg/l **	µmhos/cm 20°C
NaCl	1000	606.79	1700
NaCl	5000	3033.98	8200
KCl	1000	475.62	1700
KCl	5000	2378.00	8200

*from CRC,1979,pp.D-289,D-299
** derived by the author

Table 3

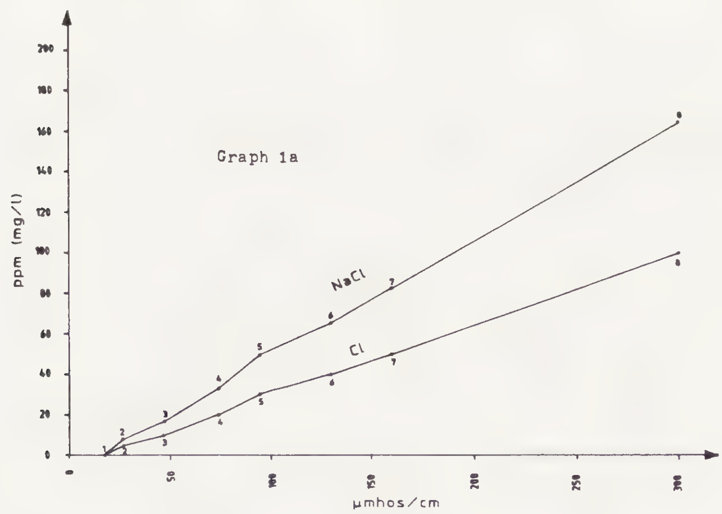
For the conversion from ppm (mg/l) to µsiemens/cm the applicability of an empirical formula was tested. The ppm (mg/l) of the salt compound is divided by an empirical factor ranging from 0.55 to

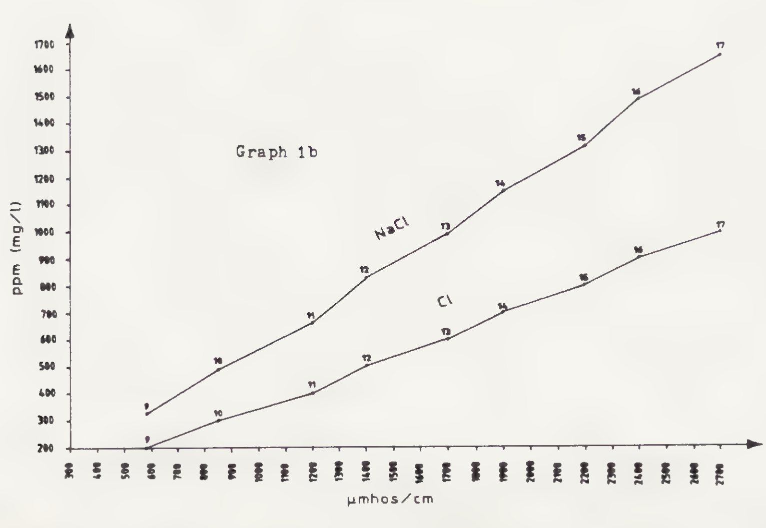
0.9 (APHA,1975,p.72). This factor varies depending on components in the water and on temperature. The µsiemens/cm and ppm figures included in Tables 1 and 2 of the comparative study were used in this formula to check the applicability of these empirical factors and formula. The results are listed under empirical factors in Tables 1 and 2. In Table 1 the factors derived by the author fall within the range of 0.55 to 0.9 for NaCl solutions greater than 164.8 ppm. In Table 2 these factors fall between 0.55 to 0.9 for KCl solutions greater than 1490 ppm. Therefore the conversion formula with an empirical factor of 0.55 to 0.9 may only be used for solutions of relatively high concentrations of soluble salts.

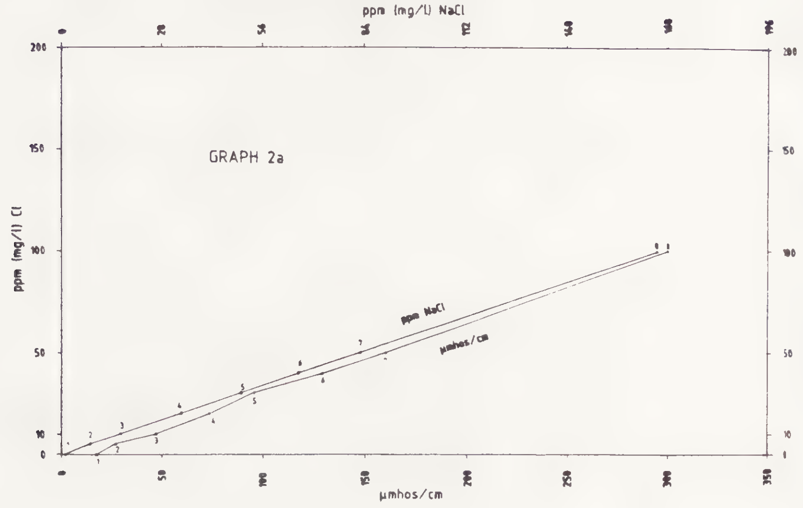
Graphs 1a and 1b compare the concentrations of NaCl and Cl solutions against conductivity listed in Table 1. The conductivity readings of the NaCl ppm concentrations are greater than the conductivity readings of the Cl ppm concentration of the same solutions. For solutions 1-8 and 9-17 the difference in ppm concentration becomes greater as conductivity increases (Graph 1a and Graph 1b). Graphs 2a and 2b compare the NaCl concentration and conductivity against the Cl concentration listed in Table 1. The conductivity readings of solutions 1-8 increase in a more linear fashion than do the conductivity readings of solutions 9-17. Upon increasing ppm Cl concentration of solutions 1-8 and solutions 9-17, the NaCl ppm and µsiemens/cm figures approach one another.

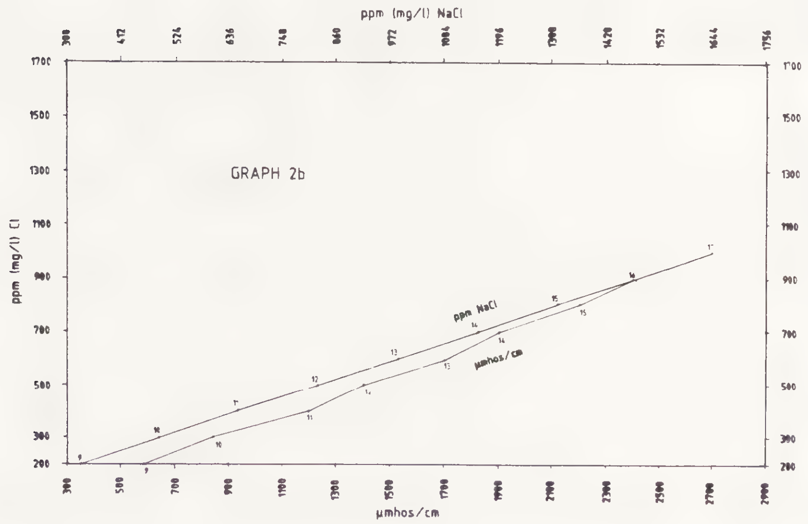
CONCLUSION

This comparative study uses one of the most common soluble salt contaminants in ceramics, chlorides, to illustrate the importance of the conversion of quantitative expressions for the salt extraction process. Each ion which forms the salt compound contributes to the conductivity of that compound. If conductivity in µsiemens/cm of all dissolved salts is used as an indication of the completion of the extraction process, the concentration of the salt compound must be used for the conversion to µsiemens/cm. Further study is required to express varying concentrations of each of the soluble salt compounds of chlorides, nitrates, phosphates, sulphates, and carbonates in µsiemens/cm of conductivity. A conversion chart for each of the salt compounds will facilitate monitoring the removal of the salts.









FOOTNOTES

1) tests carried out at the Central Institute of Restoration, Rome, Italy

2) Orion specific ion meter and electrodes available from Sargent-Welch Scientific Company
7300 North Linder Ave.
P.O. Box 1026
Skokie, Illinois 60077 U.S.A.

3) Ciolfi Scientific Instruments
Via Mercato 5
Milan 20121 Italy

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Working Group 21

Training in Conservation and Restoration

Formation en conservation et restauration

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TRIENNIAL OVERVIEW

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AIMS AND OBJECTIVES

1. To promote the training of conservators and restorers at all levels, but in particular at a professional level.

2. To increase the level of training of conservators and restorers particularly those in underdeveloped countries.

3. To provide an avenue of communication between conservation teachers and others involved in the training of conservators and restorers.

4. To provide training for conservation teachers in the methodologies of teaching conservation and restoration.

PROGRAMME 1984-1987

1. **'The Conservator-Restorer : A Definition of the Profession':**

   The definition of the conservator-restorer has been adopted by the ICOM Committee for Conservation and also by ICOM. It has been widely publicised, in particular through articles by Christoph von Imhoff, and is available in a number of languages.

2. **Conservation Students' Theses and Dissertations:**

   Gerhard Banik, Gabriela Krist and Sebastian Dobrusskin have completed their 'Bibliography of Theses, Dissertations and Research Reports in Conservation - a preliminary report'. This is to be joined with parallel reports of the United Kingdom training institutions produced by Peter Winsor, and one being produced of the North American institutions by Rebecca Rushfield, for publication purposes.

3. **The Role of Science in Conservation Training:**

   An interim meeting of the Working Group on the Role of Science in Conservation Training, was held at the British Museum, London, from 6-10 October, 1986. It was attended by 52 delegates from 15 different countries. The fourteen papers presented, along with the discussions have been edited for publication.

4. **Working Group Projects:**

   A number of projects initiated at the last Triennial meeting in 1984, coupled with projects accepted by the Working Group at its interim meeting in 1986, are currently in progress. They include:

   i. a survey of job descriptions and work standards for different levels of conservator, including conservation teachers and scientists;

   ii. survey of the availability and suitability for conservation teaching of specimen sample sets and didactic material;

   iii. promotion of the provision of training courses for (a) teaching conservation teachers, and (b) the use of didactic material;

   iv. survey of syllabi for conservation training courses;

   v. production of a register of conservation teachers;

   vi. promotion of the activities of the Working Group through the appointment of Activity Coordinators in different fields of conservation training;

4. vii. evaluation of methods for selecting students enrolling in conservation training courses; and

viii. promotion of the aims and objectives of the Working Group on Training in Conservation and Restoration.

SUMMARY

There are now 78 members of the Working Group. Three Working Group Newsletters have been published to date with financial assistance from the ICOM-CC Directory Board. In addition to the interim meeting of the Working Group in London in 1986, there have been a number of important meetings involving conservation training:

i. Conservation Training Symposium; British Museum, London, December 1984;

ii. 5th International Restorers Seminar; Vesprem, Hungary, July 1985. A similar session is scheduled for the 6th International Restorers Seminar in 1987.

iii. The 9th International Symposium on the Conservation and Restoration of Cultural Property - The Training of Specialists in Various Fields Related to Cultural Properties; Tokyo, Japan, November 1985.

iv. Evaluation of Training Courses on Conservation of Movable Cultural Property; Bogota, Columbia, November 1985.

v. Meeting on Conservation Training; Getty Conservation Institute, U.S.A., June 1986.

At the time of the interim meeting in London, disucssions were held on the proposal to establish an Association of Conservation Teachers. After much debate, it was agreed that instead of setting up a new organisation there should be stronger support and more involvement by those concerned in training, with the ICOM-CC Working Group on Training in Conservation and Restoration.

Important contact has been made with the ICOM International Committee for the Training of Personnel (ICOTP), and it is hoped that a joint meeting of the ICOM-CC Working Group, ICTOP, ICOMOS Training Committee, together with ICCROM, will be held in 1988.

ANALYTICAL CHEMISTRY FOR CONSERVATION STUDENTS

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SUMMARY

The chemical analysis of cultural materials is taught, not with the primary aim of developing expertise in any particular technique, but in order to illustrate the essential steps and some of the problems associated with the analysis of cultural property.
The course, taught as part of the Bachelor of Applied Science in Conservation of Cultural Materials at the Canberra College of Advanced Education, emphasises the need for conservators to communicate effectively with professional analytical chemists through an understanding of the full analytical process and the acquisition of a basic technical vocabulary, and to critically evaluate analytical data. The reasoning and philosophy underlying the development of the course is discussed and examples of subjects and laboratory practicals are presented.

Introduction

My perception of the educational requirements of conservation students in a general conservation analytical chemistry course is based on experience of working as an analytical chemist within cultural institutions, and teaching analytical chemistry to conservation students.

When I began working in this area, I was immediately struck by the fact that most conservators have a very poor understanding of the essential parameters governing the design and execution of analytical processes, and that this lack of understanding leads to serious problems in formulating realistic conservation programs which include the examination and analysis of cultural property. The same shortcomings at an administrative level result in poor decisions in expenditure on equipment for conservation laboratories and inefficient use of the resources available both within and outside the conservation facility.

The roots of the problem can be traced at least partly to deficiencies in the way in which conservators learn about chemical analysis, and the usual problems faced by professionals in one area in apprehending the subtleties of another specialist field. Police workers involved in examination of physical evidence are faced with a similar situation for example.

It is vital that the students become aware of advanced analytical resources, are equipped to gain effective access to them, and are able to critically evaluate the results, as there is an ethical responsibility to obtain the best information from an object, most particularly if samples are taken. Of course not all analyses in conservation directly involve objects, but the quality of analytical work has a direct bearing on the choice and execution of treatments in these cases as well.

The Analysis of Cultural Materials unit at the Canberra College of Advanced Education is a 14 week course (5 hours/week, 1 hour in class and 4 hours lab) taken in the final year by students specialising in diverse specialties such as paintings, paper, metals, textiles, objects and photographic conservation. The science course preceeding the unit consists of general introductory chemistry units (at the first year tertiary level) outside the conservation facility, which is neither related to conservation issues nor deals in detail with many of the materials and processes important to conservators. As a result, many of the students have a poor conceptual knowledge of basic chemistry, are not mathematically inclined, and are not generally conversant with the basic physics necessary to understand the theory of instrumental analytical techniques.

The unit deals mainly with the principles of instrumental analytical techniques; other methods of identification and examination which can be employed on a small scale by the conservator are covered in the appropriate conservation units.

The physical resources available for laboratory practicals at the college are quite limited, but fortunately Canberra is home to many advanced laboratories in universities and government departments, so that it is easy at least to show the students a representative range of modern facilities. In the case of the electron microscope, microprobe, XRD and XRF the facilities of the Australian National University are available for hands on use.

In summary, the difficulties facing the instructor are: the diversity of conservation specialties; the low level of chemistry, physics and mathematical ability of students; limited and generally dated teaching resources and a very short time available to teach the subject.

On the positive side, the vast majority of the students are highly motivated to conservation, intelligent and a pleasure to teach when the right approach can be found.

In the course then, the temptation to attempt to rigorously teach specific techniques has been avoided in general, the reasons for this being that:

Chemical analysis is a collection of specialist and highly skilled disciplines which require not only knowledge of technique but detailed chemical knowledge of the materials. It is unrealistic to expect conservators to become competent in this arena, particularly as most conservation analytical problems are difficult, dealing as they frequently do with complex, aged and degraded mixtures. This is particularly the case with organic materials - I generally find inorganic analyses to be less of a problem. There is quite a lot of published evidence in the conservation literature of conclusions based on rather naive analytical work, and I know that this is even more common in everyday conservation.

Too much emphasis on the limited techniques available in the teaching laboratories tends to restrict the imagination of the conservator to those methods for ever after. As an example, many conservators, having carried out a few successful identifications of simple compounds or polymers using IR spectroscopy, have an almost blind faith in the generality and simplicity of the technique in real situations. This situation is not helped by the perspective of chemistry instructors, whose experience of IR may be confined to the characterisation of relatively pure compounds resulting from organic synthesis for example, nor by the deliberate design of laboratory practicals which 'work out'. I am often asked rather optimistically to "run this through the IR and see what it is".

Finally as I have already pointed out, there isn't the time, money or resources to teach conservators to even begin to be successful analysts, and in any case they have chosen to be conservators, not analytical chemists or experimental scientists.

Important exceptions occur where techniques have a particular and routine application - for example microscopic identification of inorganic pigments for paintings conservators, the determination of magnesium in deacidification solutions and a wide range of spot-tests in all areas. These are identified and practised in the relevant conservation units. Unfortunately there are pitfalls even with some of the 'simple' methods (such as spot-tests), since students rarely become properly aware of complicating factors such as interfering species which make these methods in fact very difficult to carry out reliably and require good understanding of reaction chemistry to apply critically.

Teaching students <u>about</u> chemical analysis, rather than analytical chemistry, involves lectures, seminars and visits to outside laboratories as well as laboratory practicals - which I will regard as the most important part of the course, the aim being to enable the students to directly experience important aspects of the analytical process other than (but including) the use of the equipment.

In the development of the course three main themes are emphasised as follows:

1. That the students get a feel for the mechanics of instrumental analysis, the way in which samples have to be prepared, equipment calibrated and results evaluated. This is the usual content of analytical chemistry instruction.

2. As much as possible of the scientific and technical information and experience imparted is relevant to and useful in other areas of conservation, and related as such. The chemical and physical principles underlying analytical techniques are the same as those at work in seemingly unrelated areas of conservation practice, so the analysis unit is used as yet another opportunity to learn some basic chemistry and materials science with a practical flavour.

3. Chemical analysis is revealed as a process, involving not only the use of instruments and apparatus, but emphasising design of the analytical scheme with topics such as; is the analysis necessary, choice of method(s), the importance and expense of method development, sample handling, storage and preparation, reference materials in conservation, level of information actually required, cost/benefit, communicating with scientists, finding the right method and laboratory for the task, specialisation within analytical chemistry, literature searching, knowledge of materials and probable history of sample, and evaluating results critically. It is hoped that students leave with a realistic view of the analytical process.

In the following section selected examples of how these themes are developed in practice are given.

Syllabus

Week

1	Seminar:	Analysis and conservation
2	Lecture/Practical:	Sample Preparation for X-ray methods
3	Lecture/Practical:	X-ray Fluorescence
4	Lecture/Practical:	X-ray Diffraction
5	Lecture/Practical:	Sample preparation for SEM
6	Lecture/Practical:	SEM use
7	Lecture/Practical:	Spectroscopy (UV-VIS)
8	Lecture/Practical:	Spectroscopy (IR)
9	Lecture/Practical:	Chromatography (TLC in practical session)
10	Lecture/Practical:	Spectroscopy & Chromatography
11	Lecture/Practical:	Atomic Absorption Spectroscopy
12	Tutorial/Practical:	Open topic - finish previous laboratory work, revision and discussion of lectures/labs.
13	Lecture/Practical:	Mass-spectroscopy and visit to forensic lab.
14	Tutorial:	Students give a tutorial on an analytical method not already covered applied to conservation.

Examples of Course Content

XRD, XRF and SEM/EDXS This part of the course, which occupies just over a third of the total time for the unit, is taught somewhat differently from the rest, in that there is more emphasis on learning specific skills. We are fortunate that practical instruction is provided by specialists, who are also reasonably experienced with conservation analysis, at the Australian National University's departments of Geology (XRD, XRF) and Forestry (SEM/EDXS).

These techniques lend themselves to a more direct approach because the sample size and preparation requirements for most of their routine uses in conservation are relatively easily defined over a wide range of applications, and are thus well illustrated by characteristic examples.

Students learn to decide reasonably well the choice of method and acquire enough skill to enable them not only to work intelligently with professionals in these fields, but to carry out much of the sample preparation in routine cases. This is because sample preparation and method development is often straightforward particularly as compared with analyses of organic mixtures, and being non-destructive of the sample, the techniques are much more forgiving of mistakes. Emphasis is, however, maintained on sampling, sample storage, reference materials (especially for quantitative work), result evaluation, cost, the limitations of each method etc., rather than purely instrumental aspects. Students may be made aware of related techniques such as PIGME, PIXE, NAA, PhEEM, XPS etc., but they are not emphasised since XRD, XRF and SEM are most frequently used and cited, although one or other may crop up in a student seminar (usually NAA).

Later in the unit XRF and EDXS are compared with spectroscopic methods such as IR and UV/VIS, and it is pointed out that in the former, the narrow band widths of atomic spectral lines, computerised spectral data storage and manipulation and extensive spectral data bases, make physical separation methods generally unnecessary, whereas the latter spectroscopic techniques suffer in general from broad bands due to competing quantum events (eg vibrational levels in UV/VIS), so that organic analyses in particular, often necessitate more complicated analytical schemes.

UV/VIS A simplified theory of electronic transitions leading to UV and visible absorptions is presented. The effect of adsorption on bonds is discussed with particular reference to the damaging effects of light in this wavelength range on a wide range of materials. Reference is made to fading standards and to chemical integrating dosimeters such as Phenothiazine doped PVC film. Since the laboratory practical which follows includes a quantitative determination, as distinct from the qualitative identifications of the TLC/IR set of experiments, the concepts of determinate and indeterminate errors, precision

and accuracy are introduced along with standard solutions, calibration curves, blank solutions and simple statistical techniques such as mean, standard deviation and linear regression. This information, along with the practical experience of making up standard solutions (which many still have trouble with) is part of a set of laboratory skills that conservators should have for use in everyday practice. Other such skills for example include laboratory safety and finding information about chemicals, and these are emphasised as a matter of course.

In order to familiarise the student with the use of the instrument, a series of simple spectra of a range of UV absorbing plastic window films of various colours and reflective appearances are recorded, as well as those of common transparent materials to be found serving various purposes around museums and galleries, such as glass, mylar, polycarbonate and perspex. The conservation application is obvious, but it is different in emphasis to other parts of the unit in that it stresses environmental and preventive aspects of analytical work in conservation, as opposed to the identification of materials (the glamour area). Another theme around which I intend to develop a laboratory practical in the future, is the monitoring of treatments in progress - for example wash solutions and the kinetics of washing processes or the uptake of impregnating agents.

In the second part of the UV/VIS laboratory a hypothetical company has produced a phenol impregnated, urea-formaldehyde bonded composite board for use in museum display cases. The manufacturers claim that the board contains 16mg/gm phenol, which will not only polymerise any escaping formaldehyde, but act as a slow release biocide.

The students are asked to devise an extraction, and are given a quantity of ground-up chipboard containing various (known) amounts of phenol.

The quantitative determination then proceeds, and the final results are checked against the known figures. The background spectrum of the blank is very high, owing to co-extractives from the chipboard, leading to discussion as to how this might be remedied and then to a general session on selective extractions, partitioning between immisible solvents, and so on. It is generally appreciated at the conclusion of this practical that even such a straight-forward seeming project such as this raises numerous problems to be solved before an assay can be considered reliable. The main aim is to get across the fact that method development is generally the most time consuming, difficult, and expensive part of an analysis - this being poorly understood by non-analysts in general, resulting in unrealistic expectations (stress for analysts), cost/time over-runs and poor quality analyses.

<u>IR/TLC</u> During the first IR spectroscopy laboratory, the students learn about instrument calibration and resolution and the dependence of results on the quality of the apparatus. We are fortunate to have one quite good IR and one really awful vintage model for comparison. IR spectra of various materials are obtained, including that of lanolin and two CRC corrosion protective fluids. The spectra of the evaporative residues of the CRC products (one of which is bright blue), are almost identical in every respect - within the resolution of the instruments - with that of lanolin, and the students are left to draw their own conclusions about the identity of the greasy residue in the CRC products. Most are happy to state that the major component of the corrosion protectives is in fact lanolin. They also observe that the presence of the blue dye has no apparent effect on the spectrum, which is a useful lesson in the inability of IR alone to identify minor components in mixtures.

Exercises in the identification of various simple spectra from an IR atlas are also set in order to stress the importance and often difficulty of finding reference spectra and materials. One of the methods used is a 'simple' tree elimination flow chart for the identification of polymers, such as is very common in the conservation literature, applied not only to IR spectra, but commonly to spot-tests and solution chemical identifications. Students almost invariably end up with the wrong answers and can draw their own conclusions about the unskilled use of these schemes.

The Chromatography laboratory practical deals with aspects of TLC, including the usual theoretical concepts of retention mechanisms, distribution coefficients and so on which apply to all forms of chromatography. Solvent effects (polarity/

Van de Waals/hydrogen bonding) are illustrated in terms of the chromatographic Solvent Strength Parameter (E°) and related directly to the solubility parameters (TEAS, Hildebrandts) with which students should be familiar from previous practical work in the removal of varnishes, stability of resins, and cleaning in their conservation practice. The effects of solvent changes on retention and particularly selectivity (an important concept in solubility studies) are illustrated with a simple two component separation.

During the final part of the TLC laboratory practical(s), the TLC profiles of lanolin and the two CRC products are compared, and (surprise!) they are found to be totally different. Lanolin exhibits scores of beautifully coloured spots under visualisation with phosphoric acid, those due to sterols being particularly noticeable, while the corrosion protective TLC's reveal two or three rather boring components with no spots in common with the lanolin at all. This leads naturally to a discussion of the complexity of natural products, the dangers of the naive use of analytical techniques (IR in this case), the need for caution regarding apparently cut and dried results and the importance of a multi-faceted approach to identifications of complex materials. The absolute need for method evaluation and validation and the importance of knowing the physical and chemical basis of a method is reinforced. In this case the mixture of <u>functional groups</u> in the CRC products and the lanolin must be similar but the compounds of which they are a part, are not.

This particular practical has the added attraction that it is part of an investigation which I carried out for a cultural institution.

The effect on the students is interesting ... they are first rather confident at the ease with which the non-volatile components of the CRC products were 'identified' using IR, then discouraged at how wrong they were, and finally impressed by the challenge and complexity of real analytical work. In a very compact form the students learn a little about TLC and IR practice, important aspects of solvent theory are reinforced and the complex nature of common natural products revealed. In short they learn something about chemical analysis in real life. This approach is fundamentally very different from the usual philosophy in chemistry practicals that things should work out neatly to instill confidence in the budding scientist. Hopefully none of them will ever ask a chemist to "run this through your machine and tell me what it is" in the future.

<u>GC/MS and Field Trip</u> Mass-spectroscopy is probably one of the simplest organic spectroscopic techniques in principle, and powerful in application. It also has the advantage that in some ways it can be presented to students as analogous to the electron microprobe, with which they are already familiar. The computerised data system does much the same job of background subtraction, spectral display etc., and the spectra are themselves more characteristic than the broad bands of IR and UV-VIS spectroscopy. The low limits of detection highlight the critical importance of the selection of samples and methods of handling which do not introduce contamination. Having worked through the problems associated with the optical spectroscopy of mixtures, the power and flexibility of MS and GC/MS as a means of identifying unknown organic and organo-metallic compounds is a boost to the flagging confidence of the conservators in organic analysis at this stage.

It is important that the conservation students see a really modern and well developed laboratory, and appreciate the advantages of seeking outside help, rather than struggling away with whatever inadequate equipment and expertise is available in the conservation laboratory. Oddly enough, conservators who have graduated from the course in the past, are quite good at using the resources of the Australian National University for inorganic analyses, but are much more reluctant to seek outside assistance on the organic side for various reasons which it is hoped that the present approach will begin to address. On display in the forensic laboratory are HPLC, GC, MS, 'classical methods', various specialised forms of AA, microscopic examinations, well developed TLC identification schemes as well as vaults of illicit drugs, and refrigerators with bits of people in them - in all an interesting place as far as laboratories go.

Scientists working in the forensic laboratory face similar problems to analysts working with conservators, and are in a unique position to explain their position in relation to the demands

of their clients. This independent (and usually forthright) confirmation of the lessons of the past weeks of the unit serves to reinforce the message and to decrease the sense of isolation of conservators in the scientific world. In the somewhat incestuous and cloistered world of intensive conservation training - and later in cultural institutions - it is all too easy to become isolated in an increasingly self-referential field.

Just as importantly, the students find that most scientists are themselves interested in the preservation of cultural material, and aside from the pressures of their own work, are often keen to become involved. It is here that the conservators appreciate the value of their own specialised training in the technical, ethical and aesthetic aspects of conservation, which act as a true conservative check on the application of technology to conservation.

Student Tutorial This is intended to exercise the ability of the students to read the scientific and conservation literature surrounding a technique not already covered, and present the information clearly to their peers. In general they have a great deal of trouble finding information at their level and tend to opt for methods which are (or seem) similar to those covered such as spark emission spectroscopy, or topics like carbon dating where there is a wealth of information available at a very simple level.

Tutorials on electrochemical methods for instance are not popular, probably because they require a good understanding of solution and electrochemistry, and the standard texts are difficult. There is a pressing need for didactic material about analytical techniques, which is pitched at the level of the average conservator with some science training, and which do not rapidly degenerate into a mass of frightening formulae and equations.

Unless effective ways of attacking this problem from both ends are found - that is better and more relevant scientific training, and the production of authoritative sources of information which are accessible to most working conservators and conservation students - conservators will continue to remain locked into unnecessarily limited options for the examination and characterisation of cultural material, treatment evaluation, environmental monitoring - and ultimately conservation strategies.

MASTER OF ARTS DEGREE IN CONSERVATION OF FINE ART - NEWCASTLE UPON TYNE POLYTECHNIC IN ASSOCIATION WITH GATESHEAD TECHNICAL COLLEGE

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SUMMARY

In 1986 the conservation course at Gateshead Technical College in the United Kingdom was altered so that the award offered is no longer a College Diploma together with the B/TEC Higher Diploma in Conservation of Fine Art, but the CNAA Master of Arts Degree in Conservation of Fine Art. Reasons that led to the change are outlined and the rationale of the new course is described. A link already existed between Gateshead Technical College and the School of Art History at Newcastle Polytechnic and this link is now very much closer, although a great part of the teaching still takes place at the Technical College. Some comments are made concerning the changeover to the new course in the light of the author's previous paper 'Conservation training at Gateshead - the past ten years', ICOM Committee for Conservation 5th Triennial Meeting, Zagreb, 1978.

From 1968 a College Diploma in Conservation of Paintings was offered by Gateshead Technical College and during the years 1983 to 1987 successful students also gained the B/TEC Higher Diploma in Conservation of Fine Art, specialising in the conservation of easel paintings or works of art on paper. However, 1987 is the last year in which that award has been made, as all the students commencing the two-year course in 1986 have been registered for the Council for National Academic Awards (CNAA) Master of Arts Degree in Conservation of Fine Art. The degree will be awarded for the first time in 1988.

It is worth mentioning that ours is the only postgraduate degree of this type in the United Kingdom. Therefore there is some need for explanation as to why the change occurred when it did and for the reasons underlying the change.

The great majority of students on the Gateshead course were already graduates and the teaching staff connected with the course felt that the conservation students should obtain a national award in keeping with their postgraduate status. The course was always recognised as advanced but the B/TEC Higher Diploma, although a national award, was of lower status than a degree. The Technician Education Council that administers the B/TEC certificates and diplomas regards them as being intended primarily for non-graduates and, therefore, mandatory awards are available from local education authorities for non-graduates taking such courses. On the other hand, graduates are considered only for discretionary awards when taking B/TEC courses. Thus on the conservation course one non graduate student would receive a mandatory award while eleven other graduate conservation students on the same course might be denied any financial assistance. Apart from this problem, which meant that sometimes very promising graduates who had been selected for the course would fail to enrol at the beginning of the first term owing to lack of funds, the teaching staff had an objection to the 'technician' connotation connected with the B/TEC Higher Diploma, feeling that this implied a person who could carry out various processes but who would not necessarily display the initiative and considered judgement that we expect of our students. So there were ideological and material objections to the B/TEC national award that led to the feeling that it was not ideal for graduate conservation students.

These problems had been a cause of concern for some time, although the matter became more urgent in 1984 when the National Advisory Board, that governs Polytechnics and other colleges of further education (but not Universities) in the United Kingdom recommended that the conservation course at Gateshead Technical College should be transferred to another institution that ran a greater number of advanced courses, this being judged to be in the interests of the students. Unfortunately, the Board proposed an institution with which there was no existing link. On the other hand, there was a connexion of long standing with Newcastle upon Tyne Polytechnic's School of Art History, as one of the Gateshead conservation lecturers had contributed for 11 years to the teaching of one of the practical options for their BA History of Modern Art, Design and Film, and various Polytechnic lecturers had contributed to the teaching of art history for the conservation students at Gateshead over a similar period. In 1985, therefore, discussions were initiated between these two groups.

There was firm agreement amongst the teaching staff that, as graduates formed the majority of applicants as well as the majority of those selected for the course (usually about 90%), it would be best to acknowledge the fact by seeking to obtain postgraduate recognition for the course. This would undoubtedly give due recognition to the years of undergraduate study (always three years and sometimes four years) that they had already completed, and it was hoped this would do something to ease their financial difficulties through enabling them to obtain post-graduate awards or bursaries. Newcastle upon Tyne Polytechnic is a degree-awarding institution, which Gateshead Technical College is not, and this fact enabled consideration of submission for a CNAA award either Postgraduate Diploma (PgD) or Master's Degree (MA). The CNAA MA is regarded as being a taught degree as opposed

to MPhil, that is obtained through research, and a full-time student is often expected to complete the MA Degree in one year. Similarly, the PgD is usually obtained in a single year. There is, however, a proviso that, if students require additional time to change from their undergraduate subject of study to another area, a two-year taught MA course is acceptable. As all the students have to study fresh subjects and acquire new skills, a decision was made to submit a proposal for validation of a two-year taught course for the MA Degree in Conservation of Fine Art. It was also felt that this was most appropriate in view of the considerable intellectual abilities that these students must display in the responsible care of works of art that are of aesthetic and monetary value.

Consensus of opinion held that the content of practical conservation should remain the same, that is, occupying about two-thirds of the students' time, while supporting academic subjects would be strengthened through the contribution of a greater number of lecturers and the additional resources of the Polytechnic. The art history syllabus was augmented, the teaching of conservation theory reorganised on regular seminar basis, the second-stage work was adjusted to include the Special Project, described below, and the format of the final-year examination was altered.

The discussions, writing of the submission document and validation of the course took one academic year. It was necessary to gain the approval of the Academic Board at the Polytechnic and also that of the Department of Education and Science. The first submission document had to be ready by Christmas 1985 for the first stage of the validation procedure which was a committee stage. Following this, improvements had to be made in the submission document which was re-submitted ready for the validation visit in March. The validation committee was composed of ten people, including experts in all subject areas that are taught in the conservation course. All lecturers who were to teach on the new course had to attend at both the Technical College and the Polytechnic throughout the day of the validation committee's visit. A few minor changes, such as an alteration to the weightings provided for in the final-year examination, were requested and the suggestion that there should be three external examiners was accepted. Originally it was proposed to have two external examiners, one a conservator of easel paintings, the other a conservator of works of art on paper. The third is an art historian; it is hoped always to appoint an art historian who also works in a museum.

All things considered, the validation process went very smoothly, although the conservation staff who put in so much time and effort into writing the course document will remember the time as a period requiring a lot of extra work. The fact that matters moved so fast had a disadvantage from the point of view of the students starting on the course in September 1986, as they were selected and enrolled before the bursary committee of the Department of Education and Science could meet to consider the claim of the new postgraduate course for bursaries, so denying any of the first 12 students DES funding.

The MA course is very much one of association between two institutions. Newcastle upon Tyne Polytechnic is the degree-awarding body, so the students are enrolled with Newcastle upon Tyne. However, the Course leader is the Head of the School of Art at Gateshead Technical College where some 90% of the teaching takes place. This includes all the conservation practice and theory, conservation chemistry, history of materials and most of the artists' techniques classes. The institutions are some four miles apart and it is recognised that the students cannot be constantly travelling to and fro, so it has been arranged that they attend the Polytechnic on one day per week for conservation physics, art history and documentation and research lectures and seminars.

While at first sight it might appear that it would have been best for the entire course to move to Newcastle Polytechnic, it has to be borne in mind that over 19 years Gateshead Technical College has invested capital in equipment for the conservation studios and chemistry laboratory, and, in addition, North Dene House, the self-contained, nineteenth-century house, with its ideal high ceilings and security control, in which the conservation studios are based in the Technical College grounds, provides facilities that, at the moment, the much larger institution, the Polytechnic, cannot match. Therefore, it was mutually agreed that all practical conservation would continue

at the Technical College and that conservation chemistry should still be taught there so that this important subject would retain very close links with the practical work.

The Stage 1 examination scheme at the end of a student's first year is much the same as that for the previous diploma course in that various aspects of the student's practical work are assessed, including methods of conservation, methods of restoration, technical examination and photography and documentation. There are also examinations in chemistry, physics and art history. A student must pass all parts of the first-year examination to be able to pass on to the second stage of the course.

The examination at the end of Stage 2, that is, at the end of the course, is more rigorous than that for the previous College Diploma. There are now two 3-hour written examinations in place of the previous one, these being a written paper in conservation theory and chemistry and another in art history. In both cases, three questions must be answered in three hours. Each of these written papers carries a weighting of 10% of the final composite mark. Conservation practice is the subject of continuous assessment by conservation tutors and is also judged by one of the external examiners who views the work twice during the year. This forms 50% of the final mark. A remaining 30% is made up of the mark for the Special Project that takes the place that a dissertation would in a purely academic Master's degree.

It is felt that the Master's student should successfully integrate all aspects of the course, both practical and academic, and he or she is expected to do so in the Special Project that is marked by three examiners, who are usually lecturers in conservation, chemistry or art history. The Special Project is based on one work of art or a group of similar works that has been treated by the student during the final year of the course. It has to be a well-written and presented piece of work that incorporates, not only the conservation documentation, but a discussion of all research undertaken in connexion with it, that is, investigation into conservation techniques, analytical work and historical research. The understanding and integration of all disciplines associated with the course is considered very important and for this reason the Special Project is given comparatively high weighting.

A question may be asked as to why, when in the author's paper 'Conservation training at Gateshead - the past ten years', ICOM Committee for Conservation 5th Triennial Meeting, Zagreb, 1978 (78/22/1) it was suggested that we were likely to continue offering places to non graduates, the course has now been changed to postgraduate status. There have been a few changes over the past eight years that have led to this. Increasingly employers in the United Kingdom appear to prefer graduate conservators. This may not be universally true but it has been our experience that the graduates are more likely to be short-listed for job interviews. Also there would appear to be a trend towards more of the young people who are interested in conservation of fine art to decide upon taking a degree prior to conservation training. In one year we had two good 18-year old candidates who were given places, both of whom decided to go to University prior to undertaking a conservation course. Certainly, for those wishing to specialise in easel paintings conservation, a first degree gives a better chance of entry to conservation in England, as they are then eligible to apply for any of three courses.

In addition to the considerations mentioned above, there is the fact that over the years conservation training has become ever more demanding and the competition for positions more competitive. As a general rule over the past eight years we have found at Gateshead that the graduate students have obtained the best all-round results in practical conservation and the supporting academic subjects. The non-graduate students have usually completed the course adequately but not with the distinction of some of their graduate colleagues, often because they have to work very hard at all subjects to keep up and sometimes because they lack maturity. However, it must be said that in 1985 there was an exception in that a non-graduate, who had admittedly had some previous experience in conservation, gained an outstandingly good result which exceeded that of any of the others specialising in easel paintings in that particular year. This was an example of a student who clearly had all the intellectual ability to undertake a degree course, who had decided nevertheless that conservation was the training she wished to undertake. In the present MA degree regulations there is a clause that allows for the admission of such a student but

it is expected that such a person will already have undertaken some practical conservation work and will be able to demonstrate the ability to undertake the academic subjects.

The MA student is expected to have the intellectual ability to pursue a very wide curriculum while also demonstrating good practical ability. (A practical test is set for candidates at the admission interviews.) At the same time he or she must have the necessary patience and steady temperament together with the ability to analyse problems and apply logical solutions. Above all, one would hope to find in a graduate student in his or her mid-twenties a maturity of judgement that is so necessary for anyone in the conservation profession.

EDUCATIVE SEMINARS FOR TRAINING IN CONSERVATION - ("Simulated games") - Hanna Jedrzejewska, Solec 109A/39, 00-382 Warsaw, Poland

SUMMARY

Considered is a specific kind of seminar based on logical "creative dialogues" between participants, and serving as a training in problem solving. The idea is an element of modern mathematical methodology which has already found good application in the field of business and industry for training professional operators in management and advanced planning.

The system is universal and can be adapted well to training problems in conservation, not only as concerns planning, teaching, treatment, etc., but also for bringing together representatives of particular disciplines and helping them to find a "common language". The training is carried out on simulated situations.

Introduction

Educative seminars may be differently named (creative seminars, training seminars, business games, simulated games, experimental games, creative dialogues, problem solving seminars, etc.), but they are always a kind of exercise carried out on simulated (imaginary) situations, as a prologue to real cases. To make them effective it is necessary to keep closely to proper logical principles.

Learning on one's own mistakes is said to be a good way of gaining experience, but when done on real objects, it may lead to sad results. It also could be considered unethical. A much safer and ethically admissible way is to train the hand and mind on simulated (dummy) cases. This gives full freedom to experiment without harm to real objects.

The training of the hand on dummy objects is already a well known and applied system and serves as a preliminary to real technical operations.

The training of the brain in powers of imagination, anticipation, logical reasoning, creative ideas, advance planning, critical evaluation, etc. is usually gained in long practice on real cases. There is no returning from eventual unfortunate decisions. Preliminary training on simulated situations could greatly help to avoid, at least some, mistakes. Also, it is a faster and more organized way of developing experience than just by collecting experience through real cases, as they come along.

The system of properly organized educative seminars could also be effective in promoting co-operation between representatives of different disciplines in the field of conservation, a matter strongly postulated but still meeting with opposition (the matter of "common language").

Some details of procedures and principles are briefly considered in the following pages.

General Considerations

Theory: The system of educative seminars for problem solving by way of constructive dialogues is in fact one of the elements in mathematical methodology. It was formulated by the mathematician George Polya(1), in the first half of the 20th Century, as a part of his works on methodology and teaching procedures. The general idea is based on a logically structured dialogue between participants of the seminar. These "creative" dialogues mean a concrete discussion (exchange of ideas and concepts) ending in clear conclusions. Not just plain talking, empty disputes, or loose divagations.

The system is universal.[§] It can be adapted to many different occasions. There simply must be a case which needs to be solved and a team of participants prepared to do the work. They must develop the problem in a step-by-step procedure, building up a continuous path from the beginning to the end. Each step has to start with a definite question. It must be precisely answered. Then comes the next question in turn, and so on until the final answer can be logically produced. There may be different seminar models but they always have to proceed strictly in agreement with logical principles.

The participants: The success of a seminar depends very much on the proper formation of the working team. Some basic comments are as follows:

- the persons taking part in the dialogue must be familiar with the considered subject. They should not be unprepared fresh newcomers,
- also necessary is a true motivation, not just a feeling of formal duty to participate; and the participants should be emotionally involved in the procedures,

§ For example Dr. C.C. Abt (Cambridge, Mass.) is said to be the pioneer in introducing the system to the field of business and industry for the training of professional operators in management and advance planning, but in fact, the system of solving problems by critical creative dialogues goes as far back as ancient Greece, to the philosopher SOCRATES.

- the professional level of the participants must be reasonably even. Too great a difference may cause an undesirable dominance of some persons over others,

- the general experience of participants should correspond to the level of the case under consideration, and

- the number of participants has to be adjusted to the case. Too small a group will not have a broad enough spectrum of opinions and suggestions, whereas too large a group may cause a distraction of attention.

<u>The teacher (leader)</u>: A well experienced specialist should always be present at the seminar. He or she must watch the development of the dialogue and eventually promote things when they start to slow down or correct them when they go out of line. There is a lot of responsibility for the leader. The effective running of the seminar greatly depends on his abilities. He must be a high-level professional, a good psychologist (2) and also a bit of an actor, because the whole seminar has a theatrical character. A few comments may be added here, as concerns the "teacher":

- depending on the kind of seminar, the "teacher" may act as leader, just watching the developments, or as a teacher, giving comments, drawing attention to operative details, harmful procedures, responsibilities, <u>ethical standards</u>, etc.,

- he should not impose himself on the participants, or interfere, or want the case solved according to his concepts. The participants may have better ideas,

- he either will use a prepared scenario for the seminar or work out one for himself. Sometimes it can even be done in collaboration with the participants,

- before the seminar starts he must carefully prepare himself as concerns all relevant details and possible difficult points,

- he must himself be well interested in the case under consideration, and

- he also must remember that the most difficult moment for inexperienced people is to decide where to start. Here he must give help (be prepared in advance).

<u>The cases and the stories</u>: The term "case" will mean here the general situation, whereas the "story" will denote the scenario in detail. As a general principle, the stories should not concern real live cases, because this will obstruct the freedom of creative thinking, and may also cause some directional suggestions. The scenarios may be based on pure fantasy or borrow situations from authentic cases (3), or even concern a real case, but unknown to participants. In this last instance it could be interesting to compare (after the seminar) the original solution with the participants' conclusions. Seminars may also be arranged as a kind of competition between two separate teams solving the same story and then coming together to discuss the results.

The subjects for stories are countless. The scenarios may concern a difficult problem in conservation, an unusual kind of treatment, the planning of an operation, a museum, a laboratory, or a research project, etc. As they are made for professional specialists, students, refresher courses, museum personnel, etc., all of them must include <u>ethical</u> problems, not only in phraseology but also in a practical context. One final remark: the stories have to be carefully prepared, not just spontaneously invented!

<u>The sessions (seminars)</u>: Seminars are considered as an intermediary training between theory and practice. They may be on a high creative level for professional specialists, or on a teaching level for students, operators, administrators, etc. The proceedings of the seminar should always be well documented, either taken in written form or recorded on tape. This is not only for reference but also as a part of training in a clear consequential presentation of the course of the dialogue and the arguments presented. It may even be published afterwards for the use of a larger number of interested persons (4). Sometimes even a constructive discussion between specialists can be considered as a useful "creative" dialogue (5).

The time considered as necessary for best results is important. Single session seminars can be informative but are of only preliminary importance. There is not enough time to have the imagination well stimulated. For proper effect it is much better to have a story extending over several sessions.

Similar in intention to the seminars, but not exactly the same, are single-person cases. For competent experts this is a pastime for refreshing the mind; for students it can be used in examinations, and for any kind of self-training exercise. For reasons of principle, each new session should always begin with a recapitulation of basic ethical principles.

Interdisciplinary co-operation ("common language"): Ancient objects contain different kinds of specific information. This is concerned both with the cultural context and artistic intent, as well as with material substance - as they were originally and as they came to us. There are also different kinds of specialists interested in the particular elements of this evidence.

The dangers to this evidence are two-fold : during conservation treatment when there is direct intrusion into the object's physical substance, and in storage or on display with problems of environment, maintenance, protection and respect. Also here different specialists are involved with particular responsibilities.

On the whole, quite a lot of representatives of different disciplines are involved: conservators, art-historians, curators, museologists, artists, archaeologists, architects, physicists, chemists, engineers, etc., as well as all other persons officially responsible for the preservation of cultural heritage. Each group has its own criteria and language. They see problems in different perspectives, depending on their profession. This in turn is a source of conflict of opinions, attitudes, preferences, interpretations, etc., and is causing many difficulties.

The greatest differences are between humanists and the representatives of material science. The humanists are against the intrusion of technical trivialities into their sophisticated field of emotional nature, whereas scientists, on the otherhand, are not very enthusiastic about immersing themselves into the field of philosophical arguments completely foreign to them. They are a long way from understanding each other and often are reluctant to even try it. This could be partly explained by psychological reasons: a lack of interconnecting elements of information (2).

There seems to exist a certain kind of professional monopolism. The main interests of art historians are formal values. Artistically minded people would like to see the object as new again. Chemists look at things mostly from the point of view of atoms and molecules, and engineers believe too much in omnipotent technology without paying too much attention to the philosophy of preserving objects as documents of the past. Research scientists are enclosed in their beautifully equipped laboratories and are doing very sophisticated investigations on small perfect samples without connecting this with needs in everyday practice (7).

The conservators are left to do the "dirty work" of direct operations on objects, and of meandering in between different opinions, wishes, oppositions, concepts, etc. Competent conservators are somehow able to find their own way but they shouldn't be left alone, as sometimes happens, or treated as "lower grade" specialists. The importance of this problem has recently found confirmation in the "Definition of the Profession", an official document issued by the International Council of Museums (6).

These monopolistic tendencies are well recognized. Repeated postulates are raised as concerns the integrated responsibility of all relevant parties (8). They should all participate but don't always. They may not be prepared to understand each other, or are not interested, or simply not invited to participate.

Here comes the question - What can be done to improve the situation? The simplest way would be to introduce informative lectures into the basic syllabus of particular disciplines (9). But even this meets with opposition, especially on the part of humanistic disciplines (e.g. art history), and is admitted only in exceptional circumstances (10).

The second way is to have some good reading material adapted to the level of "outsiders" (1).

However, both ways give theoretical indoctrination. There certainly is need for a "know-how", which simply means the application of gained knowledge in real situations and in co-operation with other specialists. Here, the educative seminars seem to provide a very helpful connecting link between theory and practice, just as a training in mutual understanding, otherwise known as "common language".

In the examples of stories presented in the next section it is always assumed that the participants will represent the broadest possible spectrum of relevant disciplines.

Examples of Stories for Seminars

The examples come from the author's collection and were used in the last semester of a lecturing program for students of art history (priests expected to become guardians of sacral art) (10).

1. The long story for many sessions. The basic scenario composed in collaboration with the students was as follows:

   "In wooded hills, away from traffic and modern installations, a small completely forgotten one-storey building was discovered hidden in dense overgrowth. According to hearsay it once served as a repository for things out of use at the very wealthy monastery nearby. After World War I, the monastery was dispersed and nobody ever entered the place. Recently, interest was aroused concerning the contents of the repository. The problem was entrusted to the students' team. No valuables were expected."

   This was a very romantic story, with some emotion and challenge. Each student has received one particular stage of this operation to work on at home. Then he presented his suggestions to the whole class, with critical discussion and comments.

2. Three brief one-person stories for examination. The student received a simple case to work on at home and then presented it to the whole class. He also had to name consultants.

   Case A: "A new regional museum is being organized. There is the building, some cases available, and one assistant. The rest is up to the student". The building must be properly adapted, with storage and display possibilities. A conservation workshop has to be organized, objects collected and safety measures planned. Photo and written records are indispensable.

   Case B: "The basement of a large ethnographic museum is tightly packed with cases and loose objects newly acquired and not yet registered. As a result of fire in the upper floors the basement was flooded with water which was pumped out by the fire brigade. Now the mess has to be put in order again. The student acts as curator." This includes first-aid, photorecords, transportation, drying, cleaning, cataloguing and preparing new places for storage. Obligatory co-operation with a conservator!

   Case C: "A diplomat during his service in the tropics has collected a large number of interesting artifacts. He offered this to a museum in his country. The cases are on their way by ship." The student (as curator) has to take care of this, ensuring a safe unloading and transport, preparing a place for unpacking (great caution, things fragile, broken, infected, live unpleasant "passengers" hidden in cases, etc.). Obligatory presence of the conservator!

3. Some other suggestions for stories: There are here some additonal subjects that could be used for stories. The additional trimmings, details and pitfalls have to be supplemented according to needs.

   - A modern famous painter died suddenly. His large studio is still in a working condition. An inventory has to be made of this material, paintings protected, paint materials preserved as evidence of techniques used. Include other suggestions as concerns this unexpected inheritance.

- A very large group of stone figures stands free at the top of a building, in a rather chilly deep niche. For six hours daily the front is exposed to intense rays of the sun (Venice?). The town is near to the sea and the atmosphere is heavily contaminated with SO_2. The stone is constantly wet at the back. It is peeling and crumbly. It must be treated _in situ_ (12). A sweet problem!

- Good ideas for stories can be taken from all kinds of planning, e.g. new museum buildings, adaptations of old structures, programming storage areas, arrangement of conservation workshops and laboratories, preparing exhibitions, etc. Besides conservators and museologists also architects and engineers will be indispensable here (5).

- Another good source for scenarios is archaeology. Underwater archaeology (3) and excavations on a muddy seashore (4) especially, present a rich variety of problems; there is a lot of worry for archaeologists, conservators, technicians, scientists (chemists) and museologists, with problems and arguments for very lively seminars.

- An infinite source for exciting stories is conservation. With little ingenuity and inspiration from authentic cases it is possible to create challenging situations for all kinds of seminars, as well as including decisions on treatments and also matters of maintenance.

- Teaching can provide good subjects for stories, not only for grown-ups but also for school-children. For example, educative seminars may be arranged concerning proper ways of collecting things (13).

- For a change, a seminar may be arranged on problems of publishing, e.g. on planning a new periodical for conservators and teachers which is very informative but concise and easy to read. This includes all the motions of selecting people for the editorial board, looking for prosepctive authors, a printing office, money, readers, even for the title of the journal. Very educative and amusing.

- The simplest examples of creative considerations are in our own private life. They involve the organization of a birthday party, for example. There is a lot of advanced planning and management. Members of the family act as participants. There is, in fact, close analogy in the whole mechanism to the sophisticated professional seminars.

Final comments

It is impossible, of course, to give more than a brief outline of the educative seminars system on a few pages. Some summing up may be as follows:

1. the seminars are in fact a very effective help in different kinds of training and teaching (14). They simulate not only real situations but also real activities, thus preparing the participants to real (not simulated!) work,

2. they have a preventive importance, by making people train on dummy (simulated) cases with full freedom of learning on one's own mistakes, without harm to real situations,

3. they are a good training for creative thinking and for developing operative abilities,

4. there is an almost endless possibility for inventing different kinds of stories, for all needs and levels,

5. they shouldn't be spontaneous enterprises. They have to be well planned and prepared, with a careful selection of participants,

6. they serve as accelerated systems for improving operative abilities and experience. There is _no intention_ to make the participants become specialists in another field. The participants will only have to be able to pool together the particular elements of their knowledge, for a common benefit,

7. the educative seminars seem to be much more effective for training than all the official, "_ex cathedra_" voiced recommendations.

A comment may also be given as concerns ethics. There is the same problem with ethics as with the already mentioned training of art-historians in technical matters : a lack of operational connection between theory and practice. We have phraseological ethics (definitions and statements) and codified ethics (in paragraphs). Both of them just theory, and lots of it. Very little consideration is given to practical ethics (applied ethics), though each case has its own specific ethical parameters. In the seminars, ethics is supposed to be present all the time, not only just in theory but in practice.

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SUMMARY

The Museums Association in the UK offers professional qualifications, through its own examinations, to Conservators and Natural History Technicians. The Association does not do any training directly; training is done by apprenticeships, the students working under qualified conservators, and by Institutes of Higher Education. This paper describes the role of the Museums Association, the Certificates and specialist disciplines in which they are offered, the syllabi and examination system, the problems that exist at present and looks also at the changes that might take place in the future.

CONSERVATION AND THE MUSEUMS ASSOCIATION IN THE UNITED KINGDOM

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1. Introduction

In the UK the Museums Association as the professional association for museum staff has an examination system leading to professional qualifications. These are the Diploma, mainly a curatorial qualification but also taken by some conservators; Conservation and Technical certificates and the Natural Science Technology certificate.

The Museums Association started with the Diploma examinations in the 1930s and then came early to the recognition of the need for, and existence of, conservation and other technical skills - introducing the Technical Certificate in 1953 (1) and the Conservation Certificate in 1978 (2).

The Conservation Certificate continues as one of the main conservation qualifications in the UK and is recognised by most museums when recruiting staff and in considering them for promotion.

This paper explains the role of the Museums Association in setting the standard to be attained by technical staff, the syllabi, regulations and examinations as they exist at present and considers changes that may take place in the future.

2. The Role of the Museums Association

"The Museums Association provides syllabi, liaises with students and their tutors and conducts examinations but does not instruct or train students in either Conservation or Natural Sciences Technology."(3) This quote from the regulations sets out the position clearly. The training is done by the employing museum and its staff (mainly the senior conservator) giving an apprenticeship in the practical craft of conservation: the traditional, proven, successful method of passing on practical skills in this and many other fields. A period of full time, in-service training of not less than four years is required. The Museums Association lays down strict rules on the matter of both the supervision and the work that is to be undertaken by the students before they can be accepted (registered) to take the professional examinations. These are as follows:

"Applications for registration will be accepted only from persons who work under the direct supervision of a conservator/natural scientist who is qualified and experienced in the same specialised area of conservation/natural science technology and in a conservation or natural science technology unit which has adequate facilities for that specialist work."(3)

Also the student must be working on objects that fall into the specialist discipline and not be required to undertake objects outside that area during or after the training period. "The Certificate states for each candidate, the Conservation/Natural Sciences Technology subject for which it has been awarded. The award of a Conservation/Natural Sciences Technology Certificate in one subject area does not, however, qualify the recipient to practice in another discipline."(3) This is often seen as hard, and even unfair, on those museums who have only one conservator/natural sciences technician to care for a wide ranging collection across several specialisations. However it is essential to apply strict rules in both training and professional practice to keep up a high standard of professionalism and maintain the respect given by employers and fellow workers to the Conservation/Natural Sciences Technology Certificates. People working alone, in poorly equipped workshops on a wide range of objects cannot be expected to achieve the high standard of work required from a modern conservator and only by refusing to lower their standards can the Museums Association support the profession, encourage museums towards better practices and raise the standard of care for all museum objects.

3. The Certificates and Specialist Disciplines

3.1 Conservation

"The Certificates in Conservation are for workers who are engaged in the conservation, preservation and restoration of museum collections. Syllabi are based on the materials concerned with reference to the following disciplines:

Ceramics	Sculpture in Stone and related materials
Ethnography	Sculpture in Wood
Furniture	Stained glass
Wooden Ships and Boats	Textiles
Photographic materials	Metalwork
Science and Technology	Vessel glass

Additional disciplines may be added at the discretion of the Education Executive."(3)

Sculpture in Wood and Wooden Ships and Boats are new disciplines added in 1986. The student chooses one discipline, studies this subject and is examined in it; then if successful in the examination is awarded a certificate in that discipline only, eg, Conservation Certificate (Textiles).

Originally Archaeology, Easel paintings and Works of Art on Paper were included recently the regulations on these have been changed; this is because there are now accredited courses of conservation training provided by Institutes of Higher Education in these disciplines. For these subjects, students are expected to study at one of these Institutes. It is then possible after successful completion of an accredited course (followed by a period of no less than two years practice in a conservation unit) to present a substantial portfolio of work done after completion of the course and be awarded a Conservation Certificate. For this the student must be successful in an examination, by appointed examiners, who assess both the portfolio of work and the application of conservation theory in day-to-day working practice.

3.2 Natural History Technology

"The certificates in Natural Sciences Technology are for workers who are engaged in the maintenance, preparation, preservation and restoration of specimens and are offered in the following subject areas:

Biological sciences	Medical Science Technology
Geology	Live animal and plant management
Taxidermy"	

Regrettably there are no accredited courses of natural sciences technology training provided by Institutes of Higher Education so all potential students have to obtain employment in a museum with the facilities to train them before they are eligible to register for the Museums Association examinations.

4. The Examination System

"The Conservation and Natural History Technology Certificates are professional qualifications designed to show that the successful candidate possesses a sound theoretical knowledge and an understanding of the basic scientific principles appropriate to the chosen subject, together with a high degree of technical skill and the necessary practical experience."(3) To test this ability a six part examination is used with the aim defined as follows:

"The examination provides for a thorough examination of the candidate's theoretical knowledge, but more importantly it enables the examiners to assess the candidate's practical skills. Equally significant is evidence of the candidate's ability to apply theory and utilise skills and flexibility in the sympathetic and unobtrusive treatment of a variety of objects within the candidate's chosen field of study."(2)

Parts of the examination are:

1. A comprehensive record of museum work carried out by the candidate during the three years immediately preceding the examination. A compilation of written records and technical data accompanied by photographic and other illustrative material. Additionally a minimum of three essays written by the candidate for his/her tutor must be included.

2. A project dissertation (10,000-15,000 words) relating to the special technical project (the subject and synopsis to have been submitted by the student and approved by the Museums Association at least 18 months before the examination).

3. A three hour written paper (6 questions from 12) from the general and specific sections of the syllabus studied.

4. A three hour written paper (6 questions from 12) on any section of the specialist syllabus studied.

5. A Viva Voce examination, a formal, practical and oral test on the candidate's work as identified in (1) and an assessment of the candidate's approach to describing briefly his/her proposed conservation approach on three items or problematic themes provided by the examiners.

6. A Viva Voce examination and assessment of the special Conservation/Natural Sciences Technology project 2.

The candidate has to pass in all 6 parts to be awarded a Conservation/Natural History Technology Certificate.

5. Syllabi

There are different specialist syllabi for each Conservation and Natural Science Technology discipline; a student chooses the one relevant to the work that he/she is doing and must get this decision accepted by the Museums Association and their employer. All students have to study and be examined in a common compulsory syllabus as well as in their chosen specialist syllabus (2).

5.1 The common syllabus is compulsory for all students; subjects are:

5.1.1 General history of conservation and historical outline of the subject discipline in which conservation is to be undertaken.

5.1.2 Ethics of conservation.

5.1.3 Sources of information, organisations, people, books and journals, specialist libraries and reference collections.

5.1.4 The design, construction and equipment of a laboratory, workshop or studio.

5.1.5 Conservation requirements for display and storage areas (environment etc).

5.1.6 Health and safety.

5.1.7 Cost estimates for conservation work.

5.1.8 Analysis and evaluation of conservation materials, development of new materials and methods.

5.2 The specialist syllabi all have a similar form although, of course, the content and detail differs.

5.2.1 A general knowledge of the history of the specialist subjects and the history of techniques and use of materials is required.

5.2.2 The composition and structure of the particular type(s) of object.

5.2.3 Causes of deterioration.

5.2.4 Technical examination.

5.2.5 Chemistry and technology of conservation materials and processes.

5.2.6 Treatment: cleaning, consolidation, joining and retouching, methods of making new parts, surface treatments, treatment on site, handling and moving objects, packing, transport and display.

6. Problems

There have been disagreements between the Museums Association and the United Kingdom Institute for Conservation (formerly IIC United Kingdom Group) in the past and neither group is satisfied with the situation at present. In IIC UKG Conservation News No.7 November 1978 (4), the contents of a letter to the Museums Association were published. The points made in that letter are still relevant today:

"It should be recognised that the employment of untrained people as conservators is undesirable and that this aspect of the scheme is a transient one. Future intakes should be of trained conservators or into supervised trainee posts with attendance at formal courses in conservation."

This is the ideal to be aimed at but we are still in transition with insufficient formal courses to cover all the specialised conservation disciplines that are needed.

Even earlier with the introduction of the technical certificate, the draft explanatory notes (1) said:

"The Education Committee hopes that it may, at some time in the future, be possible to arrange special training courses for candidates for the Technical Certificate. At the present time candidates are not required to attend any course of training but are expected to have obtained the necessary knowledge and experience in the course of their normal duties."

The hopes have still not been realised and the last sentence of this quotation holds true for many conservators and all natural history technicians. This is a disappointing situation for the students, the Museums Association staff and committee members and the profession as a whole.

7. The Future

7.1 There are not enough formal courses to train conservators in all the specialist disciplines; in many disciplines there are no formal courses at all. So the reality of the situation is that the Museums Association's help for students and qualifications for conservators trained on the job as apprentices will continue to be needed. This system has produced many good conservators in the past and will continue to do so in the future.

7.2 Two new disciplines (Sculpture in Wood and Wooden Ships and Boats) have been added recently because they had developed as separate subjects in museums and the best practitioners had reached similar standards of knowledge and skill to those in other disciplines. It is anticipated that there will be other specialisations developing and being recognised in this way especially in the case of social history, industry and technology collections.

7.3 The Museums Association in April 1986 put a discussion paper on membership proposals to the membership (5) and this is still being discussed. One of the ideas in this paper was that there should be a Licentiate qualification which would be obtainable by all museum professionals not only curators and conservators/natural history technologists but also administrators, designers, educators, photographers and all other technical staff in museums. This would be in the words of the discussion document: "A licence to practice the particular professional skills in a museum context." The Diploma would still be available but would be more directed towards the acquisition of management skills and also available for all the different professional specialists. This has been described as "a licence to drive a museum" but in larger museums would not only be a qualification for a Museum Director but for section heads managing teams of specialists. These ideas have yet to receive acceptance from the Museums Association membership but move in the right direction for conservation; towards acceptance as "equal but different" in relationship to curators and not as junior partners, a situation which has caused resentment in the past as it does at present.

7.4 Another change which would seem to be going ahead is the extension of the present Conservation Certificate scheme to include staff working in private conservation units; provided that the supervision, facilities, range of work and standard of conservation match the best of those existing within museums. For a long time now, conservation units in Area Museums Services and other non-profit making institutions have been treated the same as museums; this would in future be extended to the best profit-making conservation units - recognising the standard that many of them have reached and the fact that they are training staff, some of whom have not received any formal conservation training before entering their employment.

7.5 The Museums Association has submitted evidence to the Museums and Galleries Commission working party on training (6) setting out the aim "to encourage standards of excellence in professional services across the whole range of museum activities" and commenting that "professional training has a critically important role to play in furthering this process", also the role of the Association should be "to identify the major gaps in training provision and try and ensure they are adequately filled, either by others or directly by the Association itself." The recent Museums Association Education Executive (January 1987) Training - The Way Ahead (7) suggests "a series of distance learning packages to include text, video, sound, photographs etc, as appropriate; group seminars with compulsory attendance; a series of credits to be built up for the various stages of qualifications; recognition of existing courses as exempting holders from elements of credits; a stronger emphasis on management." This will be of use to conservators as well as curators but still does not solve the problem of how the all important practical training will be provided in the future.

7.6 It can be seen that there is still more to do and that the Museums Association role is likely to continue and to develop and change in the future. It is however possible that in a very short time the United Kingdom Institute for Conservation will take over most of the work at present done by the Museums Association and that the conservation qualifications will be those accepted by both bodies.

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2. The Museums Association Conservation and Technology Certificates Syllabi, First Edition, January 1978 and Examination Guidelines.

3. Certificates in Conservation and Natural Sciences Technology Regulations May 1986 (new draft prepared by Jean Glover).

4. Conservation News No.7 November 1978 pp.2-3.

5. Membership proposals - The Museums Association April 1986.

6. Evidence to the Museums and Galleries Commission Working Party on Training, The Museums Association Council 17 September 1986.

7. Training - The Way Ahead. Education Executive. Museums Association 1987.

A BICENTENNIAL PROPOSAL FOR A PREVENTATIVE CONSERVATION WORKSHOP/TRAINING PROGRAMME FOR LOCAL MUSEUM PERSONNEL IN WESTERN AUSTRALIA

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SUMMARY

Local Museums in Western Australia have mushroomed since the 1970's. To date 160 local museums have been listed by the Western Australian Museum as being open to the public.

The resultant problems in preserving their collections and the need to establish professional guiding principles have been addressed over the past 10 years in Western Australia by the Western Australian Museum and the Battye Library, in conjunction with the Institute for the Conservation of Cultural Material (ICCM) W.A. Division, the Museums Association of Australia (MAA) W.A. Division, and the West Australian Society of Archivists.

Both the ICCM and MAA W.A. Divisions have applied for state government grants since 1983 to employ from 2 to 3 full-time professional staff, who are based at, and administered by, the W.A. Museum, to provide conservation and curatorial advice and practical assistance. However, the results of training sessions in preventative conservation offered as part of this professional service to local museums have not had as far reaching effects as might be achieved.

A proposal for a preventative conservation workshop training programme for local museums has therefore been prepared for the ICCM W.A. Division. It is to be presented to the Bicentennial Authority for consideration as a Bicentennial funded project, in the event that the state government cannot financially accommodate the same programme with the W.A. Museum's Local Museums Advisory Service.

This paper deals with the context in which the proposal is made and considers the strategy envisaged and some of the basic requirements which have been detailed in the Proposal itself.

Background

Local museums have mushroomed in Australia at a rate that has exceeded that of the U.S. per head of population.[1] The Pigott Inquiry on Museums and National Collections sees this phenomenon to be evidence of a quickening interest in Australian history and refers to it as "an unexpected vigorous grass roots movement."[2] This would seem to promise the average Australian, who is also an enthused tourist, a better opportunity to reflect on his relationship to the land and the political, social and technological machinery that has carried him to the point where he now stands.

It is understandable that, being in addition to a museum, a tourist minding centre, a bay window of local pride for districts with declining populations, and a focus for political activity and schools in a new and growing community, will, often cause good collection management to be left by the wayside. Visitors to the museum will be left to wander.

The seriousness of considering a training programme for personnel assisting local museums is born out by the Pigott report[3] indicating that such folk museums could occupy a role as important as that of the natural history collections in our major museums to date. However, there is a weakness, again described in the Pigott report, which is the inability of local museums to authenticate or document many of the historical items in their collection. And as one weakness leads to another, it is not difficult to see, that in order to compensate for this lack, the museum receives more into its collection and inevitably loses more control over what it has already acquired.

It is in this context that an advisory service for local museums has been developed by the W.A. Museum. Since 1969 this state museum has, through the Recognised Museum Programme, assisted those local museums most strongly established, to achieve a high standard of care for their collections. At present 18 museums are recognised. However, in 1984 the Museum Act was widened to include museums outside of those managed by local authorities. This has also resulted in many more museums requesting assistance. This has coincided with successive successful grant applications since late 1982 by the ICCM W.A. Division in conjunction with the W.A. Museum for funding a professional conservation service to local museums.

Surveys undertaken over a 1½ year period of over 30 local museums by Rodney Van der Merwe, demonstrated the need to maintenance and improve museum buildings and to rectify inadequate conditions of display and storage as a matter of urgency. Funding could then be sought to remedy the problems identified with respect to the building, however, other recommendations regarding storage and display were not usually acted upon.

Only the few museum staff who have taken the initiative to establish ongoing contact with the Travelling Conservator and to attend various meetings and workshops on preventative conservation, have demonstrated the ability to continue with conservation projects and have contributed largely to the general running of their museum. This fact led to formulating a questionnaire in December 1986 to help identify areas where the professional conservation service could be most effective. An evaluation of the responses to the questionnaire, as well as discussions amongst conservators and the ICCM W.A. Division Committee, have provided the impetus for preparing the proposal for a Preventative Conservation Workshop/Training Programme for Local Museum Personnel in W.A.

Strategy

The proposal has considered the following strategy in order to facilitate ongoing projects and improve liaison with specialists and generalists in conservation, as well as involve the community and other training resources.

At least 6 specialised workshops per year are envisaged. A workshop would be held over a period of 2 days at a museum in an established region, where it can fulfill the role of a regional centre for the particular workshop and projects flowing on.

Six regions, which are generally accessible by vehicle from Perth metropolitan area have been specified. These include the South West, Great Southern, South East, Goldfields, Wheatlands and Mid West. Other regions such as the North West, Pilbara and Kimberleys would require a separate survey of needs in order to develop a suitable proposal for conservation assistance.

A workshop will involve a recommended number of participating museums and, will

1. Perth
2. South West
3. Great Southern
4. South East
5. Gold fields
6. Wheatlands
7. Mid West
8. North West
9. Pilbara
10. West Kimberley
11. East Kimberley

be used as a spring board or focal point for further communication between the participating local museums. It is envisaged that the workshop will require the coordinated effort of 2 conservators, one a generalist, the other a specialist. It is the generalist who will assist with the preparation for and running of the workshop, its documentation and follow on activities. These activities would involve a visit by the generalist to the participating museum. Here the generalist would identify those accessioned items in the collection which can be treated by the methods demonstrated and learnt at the workshop. They will assist with documentation of items, condition reports, and review progress made.

It is hoped that this will generate an interest in locating other items which can assist with the research on, and conservation of, the items selected for the conservation workshop. Such information could assist with exchange of objects or their components by participating museums, or with future restoration projects.

It is anticipated that the host museum could at a later date generate further community interest in preservation of material culture. This could involve contacts with enthusiasts and other cultural organisations from within the region. The host museum could also become a resource for a training project in preventative conservation held at TAFE colleges as part of their country outreach programme.

Requirements for the proposal, in brief

The proposal to be presented to the Bicentennial Authority makes provision for employment of 2 professional staff to deal with administrative and planning functions and the practicalities of implementing the programme, as well as 1 part-time secretarial assistant.

It is stipulated that the workshop itself will require the coordinated effort of two conservators. One who is employed with the programme, and is a generalist, the other would be a specialist, and would be invited to lead the specialised workshop. The structure for funding such personnel is based on similar country outreach programmes conducted by TAFE and Arts Access in Western Australia.

Strict guidelines have been prepared for the workshop. These deal with objectives of the workshop session and conditions to be met by the conservators and the host and participating museums.

Further to such guidelines the proposal includes job descriptions; costing for wages, allowances and travel expenses; computor equipment and services; printing, photocopying and publishing; conservation equipment; photographic stores; conservation and office supplies and expenses; vehicle and accessories and running costs. Private sponsorship is being considered for major items of equipment, such as the conservation van and computor equipment.

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3. Ibid.

4. Op Cit. p. 22, 5.11.

Working Group 22

Metals

Métaux

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TRIENNIAL OVERVIEW

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PROGRAMME 1985-1987

1:0 Conservation

1:1 Stabilization

a. Removal of chlorides from iron artifacts from marine and land sites
b. Stabilization of large metal objects from marine sites
c. Modern metals and alloys
d. Ethnological metals
e. Metal/organic composites
f. Coins, armour, arms, etc.
g. Bronzes
h. Precious metals
i. Methods for monitoring treatments
j. Inhibitors for chemical cleaning and stabilization.

1:2 Protection

a. Inhibitors
b. Surface coatings for bronze statuary
c. Evaluation of success of treatments over time.

2:0 Corrosion

a. Kinetics of corrosion (all metals)
b. Effects of different environments on corrosion
c. Bi-metallic corrosion
d. Interaction of soils with buried metals
e. Prevention of corrosion
f. On-site data collection
g. Tarnishing.

3:0 Analysis

a. Corrosion products
b. Computer analysis of published data for new information
c. Documentation by X-radiography
d. Analysis of metals re technology
e. Metallurgy of metals re technology
f. Analysis of metal threads on textiles
g. Reconstruction of metal surfaces.

4:0 Other

a. History of iron conservation methods
b. Ethics of metals conservation.

SUMMARY

During the past three years emphasis has been placed on improving communication between members of the working group and those involved with metals, in general. To this end three newsletters have been published and a network of members from different countries are collating information from their region. The triennial period has seen a great many publications in the metals field and these are presently being abstracted and collated for the group members.

A special meeting was held in Fremantle, Western Australia. This was a joint meeting with the Working Group on Wet Organic Archaeological Materials and focussed upon the problems of the wood/metal composite artifact.

CHLORIDE LEACHING FROM OUTDOOR BRONZES

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SUMMARY

The possibility of rapid pitting corrosion caused by chloride corrosion stimulants on the surface or beneath the patina layer of outdoor bronzes has been a cause of concern as well as controversy among metals conservators for some years. This report describes some of the results obtained from an investigation of six bronze, monumental equestrian statues.

Specimens from these statues were analyzed with optical microscopy, EPMA, SEM, X-ray diffractometry and chemical spot tests. The results indicated that chlorides were present in a superficial layer no more than 100 microns in depth, and that they were being removed from the metal surface by the leaching action of rain. It appeared that chloride-induced accelerated corrosion was not a significant factor in the corrosion of the bronzes, and that atmospheric sulfur compounds may have played a more significant role.

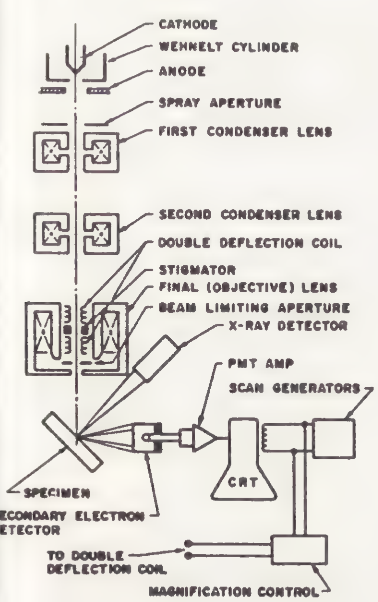


Fig. 1: The Combined EPMA/SEM (After J.I. Goldstein and H. Yakowitz, Eds. "Practical Scanning Electron Microscopy" Plenum Press, NY 1975

Introduction

The presence of chlorides on the surface of outdoor bronzes has been of great concern to conservators, since, as has been known for almost fifty years (1), this is the cause of "bronze disease". Chlorine will react with copper in the presence of moisture and oxidizers to form cupric chloride ($CuCl_2$) which under the proper conditions, can lead to a cyclical reaction which rapidly corrodes bronze through the formation of nantokite (CuCl)(2,3). Nantokite will react with oxygen to form basic copper chlorides [$CuCl_2 \cdot 3Cu(OH)_2$] and/or cuprite (Cu_2O) (which converts to brochantite) with concomitant regeneration of cupric chloride. Under the proper conditions, cupric chloride will continue to react with the metal until all of the copper has been converted. Chase (4) has demonstrated the rapidity with which the symptoms of bronze disease can appear on a clean surface in the presence of air at high humidity.

It must be noted that the environment is very important. Pourbaix that in acidic aerated systems paratacamite is formed, but where nantokite is the stable compound. In the former case corrosion is favored, while in the latter case the system may be stable. In addition, Sereda (6) has shown the importance of rainwater in determining corrosion rates, and introduced the concept of the "time of wetness" as an environmental factor.

This paper, based on a report to the National Park Service (7), presents the results of an investigation of a set of samples taken from selected monuments at the Gettysburg National Military Park. The Park is in a rural setting in Pennsylvania. The statues were from 50 to 90 years old at the time.

Procedures

Six monumental equestrian bronze statues, Generals Hancock, Howard, Meade, Reynolds, Sedgwick and Slocum were selected by the National Park Service for study. Each was surveyed with the purpose of determining the apparent condition of the metal, the different types of surfaces (original, homogeneously converted, streaked, pitted), and joins in the casting. In general, the figures were covered with a homogeneous green layer (ranging from pale to dark) typical of copper sulfate in areas where they were exposed to the weather; were dark brown to black with green or blue streaks in areas where they faced the prevailing winds (usually Northwest) but were sheltered by other parts of the statue; and were dark brown to black with blue-grey or green streaks on their leeward portions. In addition, streaks appeared wherever water could run from an upper to a lower surface. It should be noted that the prevailing winds appeared to be the major determinant of heavy corrosion, but that windbreaks or the presence of road traffic could be of importance.

Core samples and scrapings were taken, and the samples were analyzed by electron probe microanalysis (EPMA), X-ray diffraction, scanning electron microscopy (SEM), optical microscopy and chemical spot tests. The composition of the metal, the corrosion products and the presence of corrosion stimulants was determined.

Cores were taken with a 7/8" (22mm) diameter Starrett "Safe Flex" hole saw fitted with a 1/4" (6mm) arbor, mounted on a 1/2" (12mm) electric drill. The generous size of the plug was chosen to ensure that the sample would be representative of the surrounding metal, and to provide enough material for future research without having to again penetrate the monuments. The plugs obtained in this manner were cylinders of about 13/16" (21mm) diameter, with a length equal to the wall thickness of the statue, about 1/4" (6mm). There is a 1/4" (6mm) diameter hole through the center of the plug. The holes left by coring were tapped with a 1" (25mm)-12NF tap and closed with a threaded brass slug. The edges of the slug were punched in two or three places to prevent them from working loose. This method of sealing the holes was chosen in order to maintain the structural integrity of the objects until they could be permanently repaired by the restorers.

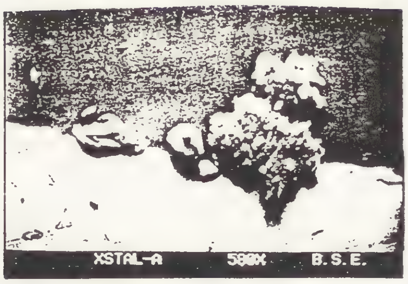


Fig. 2
Efflorescence on the Freshly Polished Surface

Subsequently, contractors for the Park Service were able to weld and shape the slugs so that they became a permanent repair.

The inner and outer surfaces of the plugs taken from the statues were consolidated with Krylon clear acrylic spray paint. After drying the cylinders were cut into three disks, showing the outer surface, the center, and the inner surface, respectively. After cutting, the acrylic coating was removed by washing in acetone several times. Samples for analysis were cut from the disks with a diamond cutting wheel using an oil coolant. After several washings in acetone, the samples were potted using a standard epoxy resin compound and polished on a Minimet laboratory polisher as per manufacturer's instructions. The grinding and polishing media were:

Silicon Carbide - 240, 320, 400 and 600 grit for fine grinding,
Metadi diamond compound - 6 micron for rough polishing, and
Gamma Alumina - 0.05 micron for final polishing.

Samples were examined with an optical microscope, a Electron Probe Micoanalyzer (EPMA), and a Scanning Electron Microscope (SEM).

The electron probe microanalyzer, also called the electron microprobe, is a device in which a finely focused (about 1 micron diameter) beam of electrons, accelerated to about 20 kV, is scanned across the target of interest. The scanned region is a rectangle about 1 sq. mm. in area. The interaction of the electron beam with the atoms of the target material causes the target to emit electrons and X-rays which are characteristic of its elements. In the electron microprobe, it is the X-rays which are of major interest. Since the X-rays are emitted from a volume only about 1 micron wide by 1 micron deep as the beam scans the target, the probe can give a highly detailed picture of the elemental composition of a small volume of material.

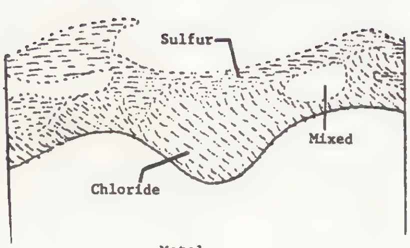


Fig. 3: HANCOCK
Right Front Leg

The emitted X-rays are absorbed by a detector and the signal is sent to a computer which does the calculations necessary for identifying and quantifying the elements detected. For this work, a Cambridge Microscan 5 EPMA operated at 20kV with a MAGIC IV, ZAF correction code was used.

The scanning electron microscope (SEM) is similar to the EPMA in that a focused beam of electrons is caused to impinge upon a target. Interaction of the electron beam with the target material again causes the generation of X-rays and secondary electrons. In addition, electrons scattered back from the surface of the target material may be detected and used to form an image. In SEM work, it is the electrons which are of major importance for creating highly magnified images. X-rays can be detected when it is desired to qualitatively determine the elements in the target.

Usually, the primary signal of interest is the variation in emission of secondary electrons from the target caused by variations in the surface topography of the sample. This allows one to observe a highly magnified image of the target with good contrast and excellent depth of field. However, when using the signal from the backscattered electrons one obtains an image which is dependent not only upon the surface topography, but also upon the average atomic number of the surface being examined. It is, then, possible to see shades of coloration which, in this case, can allow one to discriminate among areas containing copper sulfides, copper sulfates and copper chlorides. A schematic of a combined EPMA-SEM is shown in Fig.1

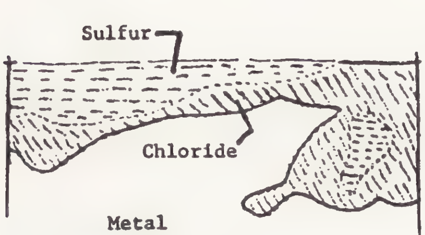


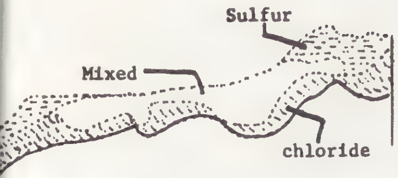
Fig. 4: HOWARD
Right Rear Leg

Optical Analysis

Observation of the metal/corrosion product interface with the optical microscope revealed the presence of green, red, brown, black and grey material, suggesting the presence of copper sulfates, cuprite, tenorite, copper sulfides and copper chlorides, respectively. In addition, exposure of a freshly polished metal/corrosion product interface to high humidity air under the microscope allowed the efflorescence symptomatic of "bronze disease" to be observed (Fig. 2) Thus, the presence of chlorides is strongly indicated.

When portions of the samples representative of the exposed outer surfaces, partially cleaned of their corrosion products by careful excavation of the pits and crevices under a stereo microscope, were exposed to high humidity air they remained stable for over five months. From these results, it may be concluded that chlorides, where present are constrained from forming atacamite or paratacamite. Although accelerated corrosion may once have taken place, the objects now appear stable, subject only to the

relatively slow process of attack by atmospheric sulfur dioxide.

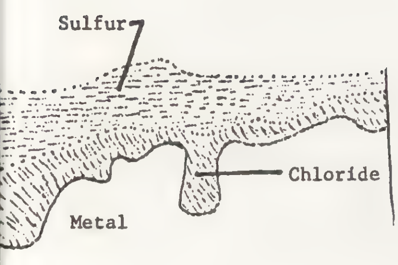


ig. 5: **HOWARD**
Left Rear Leg

EPMA Analysis

EPMA maps of the sulfur and chlorine in the layers above the metal at the metal/corrosion product interface are shown on the following pages. These maps were prepared by photographing the image generated by the selective detection of the X-rays emitted by the sulfur, copper and chlorine atoms in a small area of the interface, tracing the photographic image and overlaying the tracings. It should be noted that this technique cannot distinguish among the different sulfur or chlorine compounds that may have been present. Oxygen was not detected because its low atomic number (8) puts it in the class of elements (atomic number <13) whose X-ray yield is too low to be detectable by this technique. From these tracings we can follow the progression of the corrosion of the metal surfaces.

Samples taken from the right front leg of the horse on the Hancock monument and the right rear leg of the horse on the Howard statue are solid black (Figs. 3 & 4). They exhibit no sign of corrosion at the surface. EPMA analysis shows a sulfur-rich material overlying a chlorine-rich layer. The chlorides are in intimate contact with the metal surface. In the Hancock sample there is evidence that the chlorine has diffused into the sulfur-rich region. Since the sulfur-rich regions are black, we may conclude that they are copper sulfides. As corrosion is not in evidence, we may infer that the sulfide layer is protecting the metal, even though chlorine is present. Note that the Hancock monument is thirty-six years older than the Howard figure, yet the samples show essentially the same condition.



ig. 6: **MEADE**
Right Front Leg

As corrosion is not in evidence, we may infer that the sulfide layer is protecting the metal, even though chlorine is present. Although the Hancock monument is thirty-six years older than the Howard figure, the samples show essentially the same condition.

Samples from the left rear leg of the horse on the Howard statue and the right front leg of the horse from the Meade monument are black pitted with grey (Figs. 5 & 6). The analysis shows a sulfur-rich layer overlying a chlorine-rich layer in intimate contact with the metal surface. The Meade sample exhibits a micropit containing chlorides, while the Howard sample shows mixing of the chlorine and sulfur. In these samples we see evidence of the beginnings of the corrosion process.

We may infer that the sulfide layer has been penetrated by weathering, and that moisture has infiltrated to the chloride zone, activating the chlorides and forming pits in the metal. The grey material filling the pits is probably some combination of copper chlorides and sulfates. Nantokite (CuCl), eriochaleite [$CuCl_2 \cdot Cu(OH)_2$], copper hydroxide [$Cu(OH)_2$] and cuprous sulfate (Cu_2SO_4) would all contribute a blue-grey caste to the corrosion products.

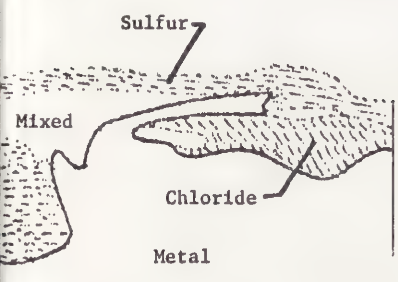


Fig. 7: **HANCOCK**
Left Rear Leg

The plug taken from the left rear leg of the horse of the Hancock monument (Fig. 7) shows a homogeneous grey-green coating. The plug removed from the right front leg of the Slocum monument (Fig. 8) is generally black, but with grey streaks. These samples are typical of the blue-grey or grey streaks and patches found on the monuments. The EPMA map of the Hancock sample shows micropits filled with chloride, a mixed zone where chlorine has diffused into a sulfur-containing layer, and an overlying sulfur-rich layer.

The micropits at the metal surface may indicate that chloride attack on the metal is still important. The grey green color is, as with the two previous samples, probably due to a mixture of copper chlorides and sulfates that have come to the surface. The Slocum sample shows a similar situation. In this case, the black may be the remnants of the original copper sulfide patina that has been undermined by corrosion products. The grey is indicative of the corrosion products having worked their way to the outer surface. In these two samples we see a more advanced state of corrosion than in the previous two samples, with converted material covering more of the surface; but the original topography appears to be retained.

The samples removed from the right front leg of the Reynolds horse (Fig. 9) and from the base of the Slocum monument (Fig. 10) are black with numerous green pits. The EPMA maps show chloride near the metal, regions of mixed sulfur and chlorine and a sulfur-rich region at the surface. The black material is probably the remnants of the original patination. It is now penetrated at many points and undermined by the corrosion products. The Reynolds

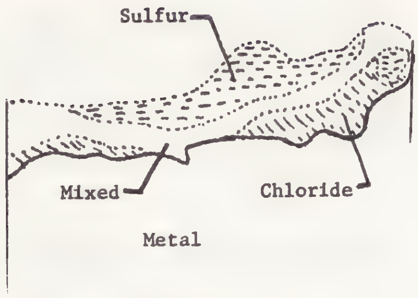


Fig. 8: SLOCUM
Right Front Leg

sample shows an area where chlorides are still forming pockets on the metal surface, while the Slocum sample shows an area where the chlorine has diffused into the sulfur-containing material.

The green color of the pits is probably due to washing by rain, which has leached away the grey material visible on the two previous samples, leaving behind the less soluble, green products. These samples indicate a more advanced state of corrosion, where a large area may be converted, but is only apparent as tiny pits on the surface. It may be assumed that when the sulfide layer has been completely weathered away, the surface will be green.

Samples taken from the bases of the Meade, Reynolds and Sedgwick statues, where the metal was well exposed to the action of wind and rain, are typical of the homogeneous, dense green or blue - green portions of all of the monuments. These samples showed very low levels of chlorine. In the Reynolds sample, the concentration of chlorine was too low to infer that the analysis was showing more than the normal chlorine background. A typical example, one of the Meade samples, is shown in Fig. 11.

The map shows a micropitted surface with small deposits of chlorine in the pits. The whole surface is covered with a sulfur-rich layer. A small occlusion in the metal shows both chlorine and sulfur, indicating that there was a path from the upper surface to a region below the surface being investigated here. There is practically no chlorine in the sulfur-rich region to the right of the metal boundary.

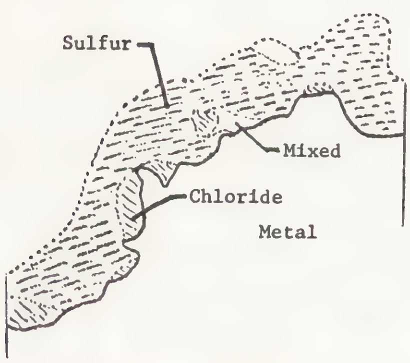


Fig. 9: REYNOLDS
Right Front Leg

These results indicate that the chlorides which were originally on the surface of the metal have been washed away by the action of wind and rain. Since the converted layer is only superficial, we may assume that the sulfates which have formed are also being washed away, and that the current exposed surface is not the original cast surface. In addition, we may infer from the highly pitted surface of the metal that chloride attack was once quite aggressive.

SEM Analysis

Polished samples were examined with either a Cambridge Mark 2A or an International Scientific Model 60 scanning electron microscope operated between 25 and 30 kV. Figures 12 to 15 are the backscattered electron (BSE) images of various samples enhanced to clearly delineate the various regions. The advantage of using BSE is that the intensity of the electrons reaching the detector, and thus the intensity of the image, is related to the average atomic number of the molecules interacting with the electrons. The atomic numbers of copper, chlorine, sulfur, oxygen and hydrogen are 29, 17, 16, 8 and 1, respectively. Thus copper sulfate with the lowest average atomic number will appear black, while copper sulfides and chlorides will appear very bright. Shades of grey will result from mixtures of the various materials. The dark region at the top of each photo is the epoxy potting compound.

Although the SEM cannot distinguish between the copper sulfides and the copper chlorides, optical microscopy and the EPMA have shown that the sulfide layer is farthest from the metal surface, while chlorides are nearest the metal. In addition, what appears as shades of grey on the SEM may be mixtures of sulfate, sulfide and chloride. This mixing of the sulfur-rich and chlorine-rich zones has been demonstrated on the EPMA.

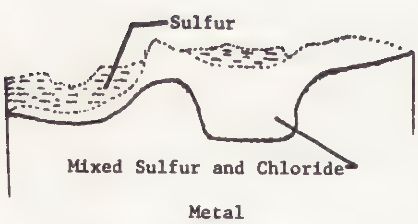


Fig. 10: SLOCUM Base

Figure 12 shows a region in which a copper sulfide layer overlays a region in which copper sulfide is mixed with copper sulfate (and chlorides). Small pockets of copper chloride are seen below the intermediate layer at the surface of the metal. In this example, the sulfate which is growing beneath the protective sulfide layer is being generated by air, moisture and sulfur dioxide that can penetrate from corrosion products present on the left and right sides of the sulfide. Note that the regions of unmixed copper sulfate are not always directly in contact with the chloride pockets. This indicates that the diffusion of chloride into the converted layer may produce copper sulfate at the expense of copper sulfide. It may also indicate that the copper chlorides are being leached through the sulfate by moisture.

Figure 13 shows a condition in which the protective sulfide layer has been breached in many places. Fingers of copper sulfate are growing through cracks in the sulfide. Much of the surface consists of mixed sulfide and sulfate. Of particular interest are the pockets of chloride directly in contact with both metal and

sulfate. This may indicate that the sulfate is growing from the chloride pockets. However, there are grey regions contiguous to the chloride pockets which may indicate the diffusion of chlorides to the top surface.

Figure 14 shows a more advanced state of corrosion, with copper sulfate surrounding what is left of the copper sulfide layer; chloride pockets in contact with both metal and copper sulfate; and a large proportion of mixed copper sulfide/sulfate (and chloride).

Figure 15 shows a surface in which the sulfide layer has been completely penetrated. The bulk of the material is mixed copper sulfide and sulfate (and chloride). A rather thick layer of chloride is seen at the metal surface. This may indicate a situation in which the sulfide layer was lost by abrasion, sulfate has been formed by the action of atmospheric moisture and sulfur dioxide, but little diffusion of the chlorides have occurred because of little contact with water.

From the above discussion we may conclude that the corrosion process can advance from the metal surface outward, even under a protective layer, if the protective layer has become cracked and fissured.

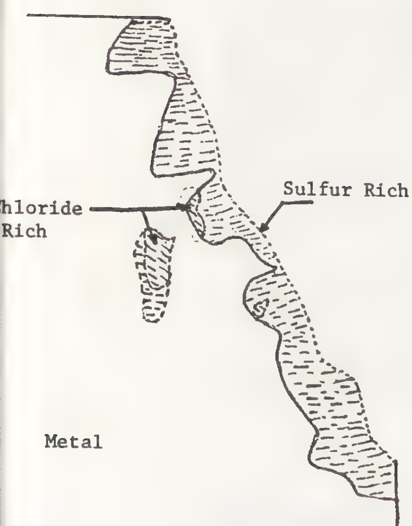


Fig. 11: Map of Meade's Base

Conclusions

The preceding discussion strongly indicates that the corrosion process is one in which:

1. The sulfide layer applied during the original patination must be penetrated by wind blown debris in order to allow moisture and oxygen to reach the bronze or the chlorides formed during the original cleaning with muriatic acid, (dilute HCl),
2. Reaction of the chlorides with the metal, in the presence of moisture and air, leads to pitting attack and the formation of copper chlorides and other corrosion products,
3. The soluble material diffuses to the surface, where it is slowly washed away,
4. Reaction with atmospheric sulfur dioxide converts some of the products to sulfates, and
5. Eventually, the chlorides are removed and insoluble products, e.g., brochantite [$CuSO_4 \cdot 3Cu(OH)_2$], are formed.

It should be noted that, as Vernon reported some time ago (8), it takes about three years for soluble copper sulfate to convert to insoluble brochantite. If during that time the surface is exposed to rain, soluble material will be washed away and the corrosion process will continue as fresh surface is exposed to sulfur dioxide.

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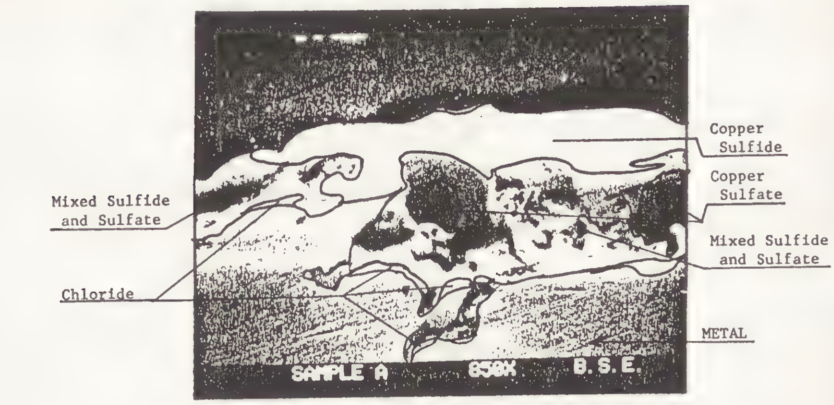

Fig. 12: CuS layer Over Mixed Sulfates and Sulfides

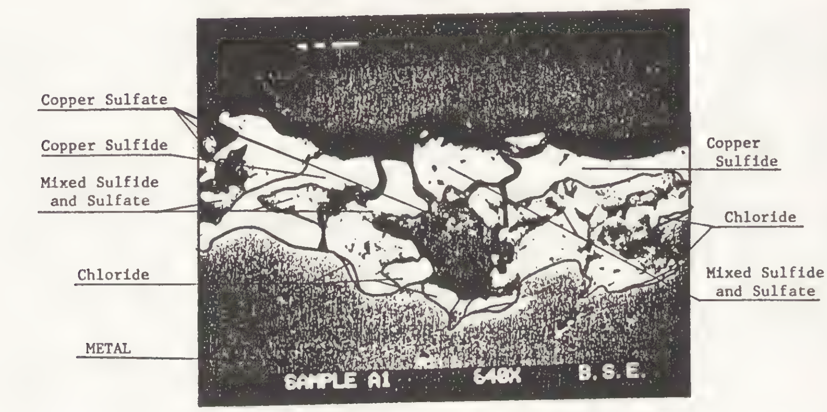

Fig. 13: Copper Sulfate Growing Through Cracks in the Sulfide Layer

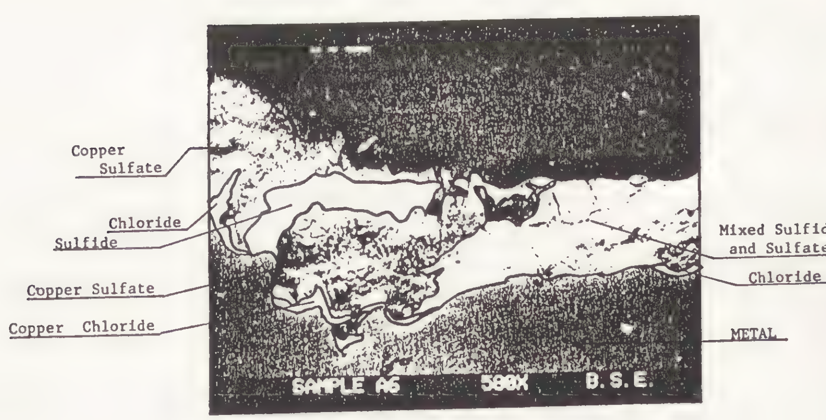

Fig. 14: Advanced Corrosion

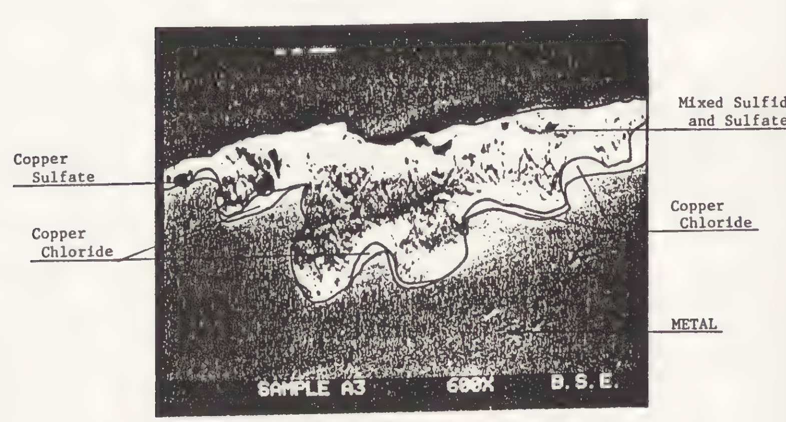

Fig. 15: Complete Conversion

Microbial Corrosion and Museum Iron Objects

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Summary

The corrosion layers of soil excavated objects often depend on microbial activities in the soil. The metabolism of the microorganism often undertake electrochemical processes and in that way, cause corrosion.

Introduction

The problems of microbial corrosion on iron constructions, in soil, have been known since about 1900. But it is not until recently that it has been possible to penetrate more deeply into this field. Still many questions remain to be answered.

In the conservation context, microbial corrosion had not been considered as a very important part of the corrosion problem. Some exceptions do exist. Microbial corrosion is described by Brinch Madsen H. (1977), Sperber E. (1980) and Hamilton D.L. (1976).

Experimental and Analytical Techniques

During the period January, 1982 to September, 1985, all conservation baths at Tromsö Museum (TM), Norway were analysed using Ion-chromatography (Dionex 10) to determine the Chloride content. At the same time lots of other anions were determined (see Figure 1). Total iron was determined by Atomic Absorption Spectrometry (AAS) in an Air/Acetyl flame (Perkin Elmer 603), from the same extractions. Samples of the amount of ions extracted during conservation, are given in fig. 2. Organic matter in the extracts was determined for about 50% of the objects in the same way as organic matter is determined in soil analysis loss of weight between 105°C and 550°C. Only 10% of the weight loss is estimated to be water of crystallisation. Somewhere between 2500 and 3000 iron objects excavated from soil were treated during this period in many different ways. This report is based on all of these analyses. Crystallographic analysis of the corrosion layers was not carried out because the inorganic products from microbial activity is either amorphous or microcrystalline Townsend (1973) and therefore not detectable by crystallographic methods. Another aspect is that the corrosion layers are very inhomogeneous.

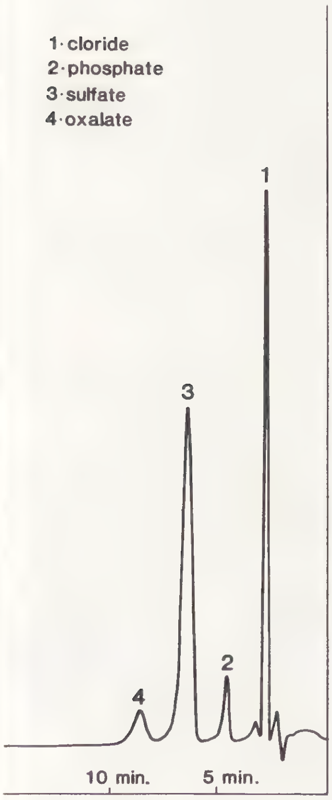

Fig. 1

Sample of Dionex Ionchromatogram The sensibility of chloride is about 5 x the sensibility of sulfate. Sulfide is not detectable on Dionex 10 Ionchromatograph.

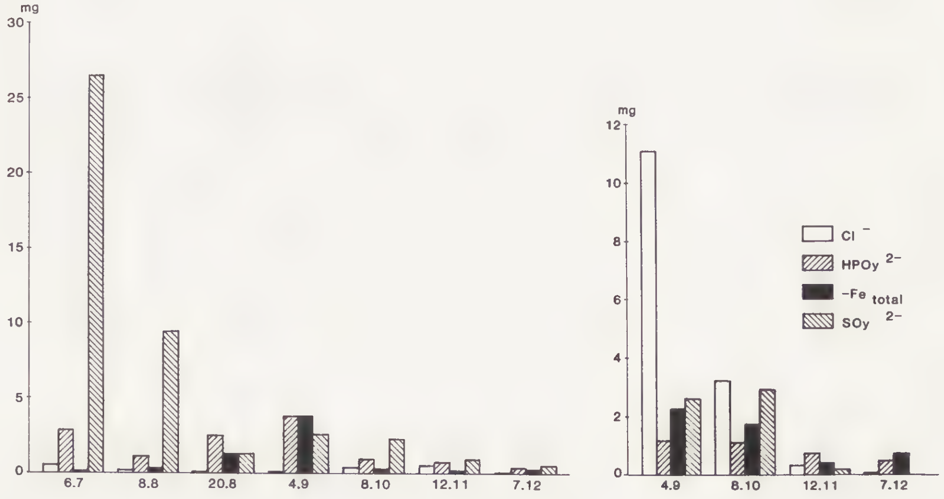

Fig. 2
Histograms - visualising the ion content of two extraction series. As normal there is no connection between the amount of ironions and anions in the conservation extracts. $SO_4{}^{2-}$ was just as well as Cl^- the dominant aggresive ion. In most cases (not shown here) phosphate was the dominating anion.

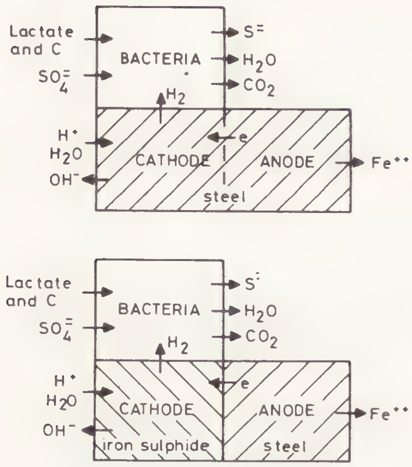

Fig. 3

Schematic representation of the classical mechanism (top) and alternative mechanism (bottom) of microbial corrosion under anaerobic conditions (after King and Miller (1971))

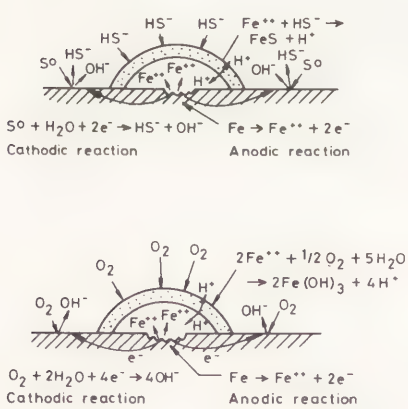

Fig. 4

Comparison of autocatalytic pitting mechanisms of oxygen and sulphur consentration cells (after Schaschl)

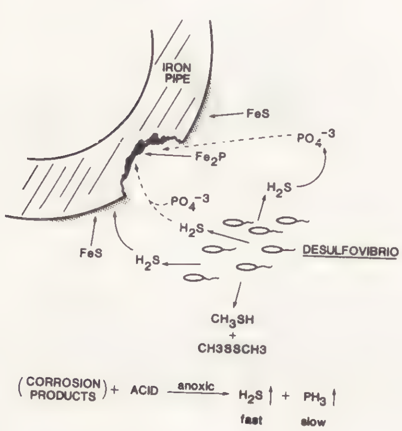

Fig. 5

Schematic of anaerobic corrosion mechanism. (After Iverson)

Theoretical conditions for Microbial Growth

The most important criteria for microbial activity of any kind is the presence of elements needed for the metabolism of the microorganism itself.

The basic elements are given by Alexander M. (1977) and Miller J.D.A. (1971). These are:

1) Carbon present as organic molecules or CO_2
2) Nitrogen present as amino groups or nitrates. There are even microorganism which use N_2 from the air.
3) Phosphorous compounds
4) Water
5) Oxygen rich (aerobic) conditions, or oxygen free (anaerobic) conditions.

The organic fraction of the material extracted from iron objects at Tromsö Museum is between 20-70% of the total extracted material.

Phosphorous is the most dominant anion extracted from the corrosion layers. Even when it is only present in small quantities it is present in sufficient quantities for microbial growth.

Lots of extracts have shown the presence of nitrate but the quantity has been calculated. Two determinations done on corrosion products, by HNC analyser, by Norsk Hydro Research Division, gave as a result 430 µg nitrogen and 680 µg nitrogen, respectively for each gram of corrosion product. Besides, humus often contains protein remnants, Bohn H.L. et al (1979)

Of 50 objects tested for sulphide, 50 gave a positive answer. This indicates that in one stage of the deterioration process, the material had been in contact with sulfate-reducing bacteria (SRB). At the same time, sulphate was almost always found in the extracted solution.

Water is difficult to remove completely when hygroscopic elements such as humus are present, Schnitzer (1976). Humus is the name of unidentified organic substances present in soil.

The conclusion is that all elements necessary for the growth of microorganism such as bacteria and fungi are present. Which of these elements (nitrogen, phosphorous or carbon) are most essential is not important in this context. King et. al. (1977) has found that sediments high in organic material, nitrogen and phosphorous, are more corrosive than sea water. Another aspect is that the corrosion damage and the cause of this damage can be physically separated from each other.

Microbial Induced Corrosion

In spite of all modern analytical techniques and great efforts, detailed information of the corrosion processes induced by microorganisms is not yet known. Lots of studies have been and are being carried out on the topic. Some are listed here: Costello J.A. (1969), Iverson W.R. (1981,1983, 1984), King R.A. et. al. (1971, 1977, 1977 , 1980), Jörgensen (1977), Ashton S.A. et al (1973). Lam K.W. et al (1984), Adams A.E. et al (1983), Miller J.D.A. (1971), Fisher K.P. et al (1981), Tiller A.K. (1984), Scott O.V. et al (1984). The conclusions of these studies is clear. Due to microbial activity metal salts are formed (see figure 3). The next step is:

A) The metal salts are removed (dissolved through ion exchange or mechanically) and more metal salts are formed on the surface.
B) The metal salts remain and cause either electrolytic- galvanic, or consentration cell corrosion.

Very often parts of the metal salts flake off and the metal surface is partly in contact with corrosive salts and partly not, concentration cell corrosion fig. 4 is the result. Local corrosion cells will give pitting corrosion.

The fig. 3 indicates the production of CO_2 and H_2 gases caused by the bacterial activity. Hamilton (1976) described how hydrogen gas when coming in contact with graphite inclusions in the iron structure form the Hydrogen Electrode Cell and then cause corrosion inside the structure. Krefting A. (1892) described experiments where chlorides accelerate a corrosion process which in this case depends on carbon dioxide. Smith et al (1975) conclude that one of the reasons why iron sulphide is so corrosive is that, as for chloride salts, it has good electronic conductivity properties.

Bacterial Corrosion

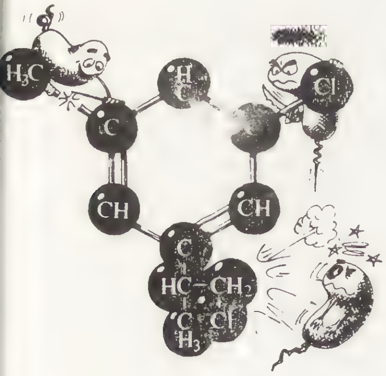

Fig. 6

Microbial break down of organic matter (after Ormerod)

The most studied group of microorganisms causing corrosion are at the moment the sulphur reducing bacteria containing species such as the Desulfovibrio group. Species such as Thiobacillus and Sulfolobus are sulphur oxidizing bacteria. Corrosion due to E-coli bacteria is described by Ashton et al (1973). That microorganisms live in symiosis with other microorganism, as described by Hamilton W.A. (1983) and Tuovinen O.H. (1980)

"Tubercle deposits collected from pipelines in the Columbus, Ohio, distribution system and examined for their microbiological, chemical, and mineralogical composition were found to contain several kinds of organisms, including sulfate reducers, nitrate reducers, nitrite oxidizers, ammonia oxidizers, sulfur oxidizers and various unidentified heterotrophic microorganisms."

Theoretically, the presence of SRB should make it impossible for objects from marshes, pits and other water-saturated surroundings with lots of organic materials to survive long burial times. Often these finds are very stable due to iron sulfide and vivianite layers. The poisonous effect of iron sulfide on SRB is described by Iverson (1983). Leadlay (1978) describes ferrous ions as a co-enzyme catalysing the microbial activities. It seems that only objects where SRB activities have been hindered by the precipitation of iron sulphide have survived. Iverson has described another corrosion procedure (1984), (see fig. 5) where SRB participate without being able to tell when the system will go in this or that direction. The bacterial activities are, together with salts dissolved in the ground water and organic ligands aggregates, building the corrosion layer present at the time of excavation.

Another problem is that when excavated the objects with its salts and organic matter is exposed to oxygen, microorganisms and water vapour present in the atmosphere. The already existing salts will more easily give rise to electrochemical corrosion. Cracks in the corrosion layers will make an uneven penetration of oxygen into the metal surface giving rise to concentration cell. New microorganisms will come in contact with organic matter and help to break it down (see figure 6) In this way inorganic ions like sulphates, sulphides and chlorides which are bound in the organic fraction, are liberated.

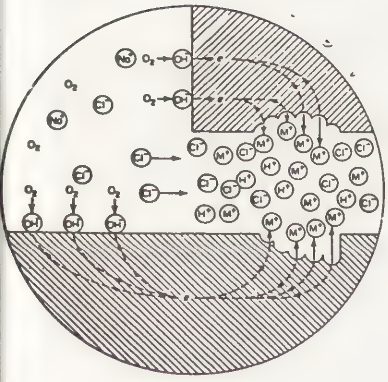

Fig. 7

Pitting/Crevice corrosion (after Bardal)

Corrosion is an electrochemical reaction and as long as the chloride irons are not undergoing a process of the type $Cl^- + e^- = \frac{1}{2} Cl_2$ it is not a part of the electrochemical process itself. The participation of the chlorides ions in the corrosion process are purely by precipitation and/or hydrolysation of ferrous ions as shown on fig. 7 and 8. Chloride ions are more like a catalyst or accelerator.
Opposite the microbial reaction which are electrochemical, the chloride does not cause the corrosion process, it only speeds it up.

The reason why all these bacteria exist is that they are part of the earth's recycling system. They are specialists in breaking down. We can't stop it, only slow down the speed of disintegration.

Conclusion

Corrosion caused by microorganisms is not easy to measure and has no distinct separation from galvanic corrosion caused by inorganic salts. To deny or neglect their presence is dangerous but easy. Nature does not treat pieces of historical value different from other specimens.

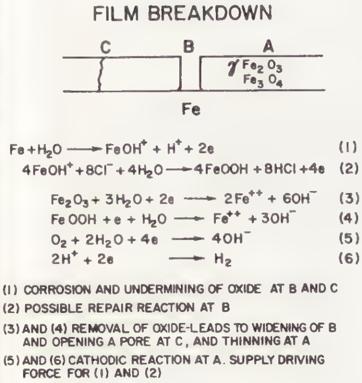

Fig. 8

Generalized picture of film break down (after Cohen)

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THE IMPORTANCE OF MATERIAL TESTING: RESTORATION OF A ROMAN HARNESS

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SUMMARY

Rescue excavations by the Veszprém Museum of a Roman horse grave yielded a bronze harness assemblage. Conservation treatment of the material was performed, based on a detailed analysis of the objects to get the maximum information possible on the method of production, as well as the treatment necessary for the objects. The finds were investigated by binocular light microscope, and in a water vapour chamber. Provisional treatment of the objects were performed in an ammoniacal potassium-carbonate solution further analysis of the objects included a chloridetest, and X-radiographer exposures. Corrosion products were analysed by spot tests as well as X-ray diffraction; the basic metal alloys were investigated by spot tests, spectrographical and metallographical analyses. The above investigations yielded unambiguous data on the production of the harness the quality of the alloys used for the production as well as invaluable data concerning the proper concervation treatment to be followed. Based on the scientific data, we could reject wet and chemical treatment of the objects, because these would probably detach the corrosion layer preserving the original surface. This corrosion layer was stable, resistant and of uniform distribution.

1. Introduction

During house-building a Roman horse grave was disturbed by an excavator; the find was reported to the Veszprém Museum and duly unearthed by its archaeologists. Among the finds there were disc-shaped and pierced strap distributors, half-round-headed buttons of different size, a curb with barnacle, and leather remains in a rather fragmented and deteriorated state.

When restoring the finds one of the aims beyond conservation was to apply material testing as comprehensively as possible. Material testing was intended to supply relevant data on historical authenticity and the techniques applied as well as to provide information concerning the manner of treatment.

2. Description of finds

The recovered finds were perceived to be in good condition, although most of them were covered by an apparently thick bluish, greenish corrosion product. When held in hand, the relatively heavy weight of even the smaller buttons was conspicuous. In the case of thinner objects deterioration through corrosion was more significant and reached more deeply. In some instances there was such a mass of corrosion products that their separation could take place only after the tests had been carried out and even then only by meticulous mechanical procedures.

On close inspection the objects were found to be covered by a relatively even grey surface layer. By way of a thorough examination it turned out that the objects in question were made of yellow bronze material and not of tin. In the course of material tests one had to pay more attention to the observation of this layer and be on the watch for silver or tin coating on the original surface.

The essential items of horse trappings were made of leather. As for this find, leather remains have survived only in places where the corrosion products "conserved" them, in a completely brittle and crumbling state. The testing of these leather remains did not take place since their quantity was minimal, and it seemed impossible to examine either the grain or any tanning agent.

3. Material tests

In order to achieve the aims described in the Introduction the following tests were carried out:

- 3.1. Visual examination under binocular microscope
- 3.2. Testing in vapour chamber
- 3.3. Preliminary treatment with ammoniacal potassium carbonate
- 3.4. Chloride test
- 3.5. X-radiography
- 3.6. Examination of corrosion products
  - 3.6.1. Spot analysis
  - 3.6.2. Spectrographic test
- 3.7. Examination of metal alloys
  - 3.7.1. Spot analysis
  - 3.7.2. Spectrographic test
  - 3.7.3. Metallographic examination

3.1. Visual examination under binocular microscope

Inspecting the bronze objects with the help of the unaided eye as well as under the binocular microscope, there was an evenly distributed grey layer to be seen underneath and next to the coloured corrosion layer. When removing this layer the base metal under it was found to be yellow bronze. After the upper layer of corrosion products was similarly removed, no metal coating or its traces - indicating the presence of silver or tin - were discovered. It was established, however, that the above grey layer has retained the original surface and its texture for most of the objects. The reverse side of one of the strap distributor discs has still preserved the traces of shaping by a file after casting.

3.2. Testing in water vapour chamber

Searching the objects for compounds which become activated when exposed to high relative humidity, was carried out in water vapour chamber. This is a well-established complementary method in the treatment of bronze objects.[1]
For this purpose it is best to use a glass desiccator filled with water. The objects which were placed on a porcelain tile and sealed were observed after the elapse of 24, 48 and 72 hours. Inspecting them afterwards under microscope no transformation was detected on the surface of the objects. The chloride test carried out later proved that the objects contained no active chloride compounds.

3.3. Preliminary treatment with ammoniacal potassium carbonate solution

So far the best preliminary method to be applied when the presence of a further metal coating was suspected has been the employment of ammoniacal potassium carbonate solution.[4] In this case, however the results were unsatisfactory. The "protective layer" or patina mentioned above had been considerably loosened by the alkaline solution and, accordingly, any further treatment of this sort had to be given up. No silver or tin coating, or any traces of them were found.

3.4. Chloride test

The objects were stored in distilled water for 4-5 days, and the resulting solution was used to check the chloride content. A small amount of the solution was heated during the day and examined in the morning when cold, acidified by nitric acid and with a drop of silver nitrate added to it.[1] The results of the tests were negative

Already at this stage it emerged that there might not be any means of applying wet, chemical cleaning, since the above grey layer - which was not to be removed as it preserved the original surface - became brittle when boiled in distilled water. The absence of chlorides was quite reassuring from the point of view of the objects' future stability.

3.5. X-radiography

One of the local companies where X-radiography is used to check welded joints generously offered help. Information concerning objects like the one mentioned above - where corrosion products and textile remains held several fragments together - could be gained from X-ray photographs only /the photos were taken at 1, 3 and 4-minute exposure times, 5 mA current intensity, 120 and 140 kV voltage/.

The shape of the metallic fragments in the lump was outlined on the film. One of the pieces, which was later separated by mechanical means, proved to be a crucial detail in assembling the curb. The above-mentioned textile remains were brittle fragments saturated by iron corrosion and were not suited for fibre test or other examination.

3.6. Examination of corrosion products

3.6.1. Spot analysis

The application of spot analysis has been spreading recently since it is a microanalytical method which can be carried out in a relatively short while. It does not require expensive appliances, the amount of the sample needed is very small, moreover the sample can be dissolved on the surface of the metal objects and the traces of the treatment can be easily removed afterwards.

In the course of the analysis the methods applied by Zoltán SZABÓ[3], were employed. Further on I used the very useful recipes found in Fritz Feigl's book[5] as well as the ones reported on by Marilyn Laver[6] in her Zagreb lecture. Below only those details will be discussed whose application in restoration is not known yet or has not spread widely. A detailed description of the methods may be found in Note 1.

The reactions of silver, Ag could not be evaluated with any certainty since the high lead content discovered later disturbed its detection The sample dissolved in cc HNO_3 gave positive results for allmost all characteristic reactions of lead, Pb. Since it is possible to detect iron, Fe from the very same solution, it was examined to this effect. The presence of iron is not surprising and gave positive results when various methods were applied since the solution of the corrosion products of the mouthpiece and other iron finds as well as the iron content of the soil had worked their way into the

pores of the corrosion layer covering the finds.

Bismuth, Bi could not be traced by the reactions listed, probably because of its presence in a small quantity only. Later on, however, spectrographic analysis proved its presence. For the detection of arsenic, As which is a common ingredient in ancient bronze objects, practically the only experiment available is the Gutzeit-test. The slightly positive results were not borne out by subsequent instrumental testing. A further sample fragment was dissolved in cc HNO_3 in the presence of tartaric acid so as to confirm antimony and tin. The presence of antimony, Sb could not be firmly established relying on the positive reactions only, since they brought about positive blank tests with tin ions as well. The tracing of tin, Sn was successful both by cacotheline and phosphorus molybdate paper.

Dissolving the rest of the sample in hydrochloric acid it is possible to trace further cations in the solution /Ni, Co, Zn/. The presence of nickel, Ni or cobalt, Co could not be established beyond doubt by dimethylglyoxime. When trying to trace zinc, Zn beside the well-known and fairly complicated method dithionic solution in CCl_4 may prove to be a successful test, although several other ions defined so far show the same reaction. The presence of zinc in a significant amount, however, was beyond doubt established by instrumental analyses.

The importance of the grey layer has been referred to above; when examining it special importance was attached to the detection of lead and positive results were obtained by each of the available methods. In addition Fritz Feigl's method[5] /p. 437. 12/, which is applied in criminal investigations to establish the trajectory of the bullet was also utilized. The latter method will distinctively trace even the smallest amount of lead. A detailed description is included in Note 1.

Similar results were obtained while using a recent method for the examination of tin. In Zagreb my attention was caught by M. Laver's[6] presentation of a method whose brief outline is shown by Diagram 1. In this case the surface sample needed is provided by an external electric source. This method may be effective even when other reactions are negativ /description included in Note 1/. Under the action of electricity the deep-blue colouration that proves the presence of tin was inmediately recognized on the paper impregnated and treated by phosphorous molybdate /Feigl[5] p. 108/ When applied to trace iron the same method /Feigl[5] p. 161/ provides satisfactory results on test paper /Note 1/.

Summarizing the spot analyses of the corrosion products it may be stated that the assumption of a relatively high quantity of lead in the coating preserving the original texture was correct. The presence of lead on the surface and in the corrosion products also confirms that the base metal must have had an even higher lead content. High lead content may be dangerous when chemical procedures, e.g. alkaline dechlorination is applied, since it may be dissolved from the alloy thereby weakening the object.

3.6.2. X-ray diffraction examination

The aim of X-ray diffraction examinations is to determine the structure of the corrosion products found on the objects. The mineralogical department of the local university generously undertook the carrying out of the necessary investigations free of charge.

The majority of the corrosion products evolving from the components of the bronze alloy are present on the object in a crystalline form. It was decided that as a suitable procedure the Debye-Scherrer X-ray diffraction method would be applied.
The preliminary results showed that the most important task was to get to know and identify the structure of the layer or coating, as well as that of the ones beneath it. Fragments which have flaked off the surface of one of the objects and were impossible to place back were found to be suitable for the purposes of such an examination which also provided an opportunity to separate the various layers.

The surface layer showed that the bulk of this substance - more than 90 % - consisted of lead carbonate /$PbCO_3$/. The remaining ingredients were present in such small quantities that their further analysis was not deemed feasible.

In the course of the analyses 4 different layers could be separated proceeding from inwards to outwards. When the

diffractograms of the four layers were placed next to one another, it occurred that starting from inside the amount of lead carbonate rose evenly and in the outermost layer it surpassed the above mentioned 90 %.
Relying on these findings it can be stated that the compound /lead carbonate, $PbCO_3$/ found on the surface of these bronze objects may be considered a protective layer since cerussite /white lead ore/, which is natural lead carbonate, is not soluble in water /cerussite is, in fact, white, its grey colour may have been caused by some impurity in this instance/. This lead carbonate might become Basic lead carbonate /$Pb/OH/_2 \cdot 2PbCO_3$/ which may perfom the function of a protective layer according to Schläger[1] /p. 37/. Furthermore it may be established that the transformation of the compounds would endanger the aesthetical appearance of the object. After careful and thorough mechanical cleaning the objects have to be consolidated by a synthetic resin solution that is sucked through. Following this they have to be treated by waxing so that their optical appearance should be satisfactory.

3.7. Examination of metal alloys

3.7.1. Spot analysis

The examination of the base metal was carried out simultaneously with that of the corrosion products. Taking samples from the base metal is usually a more complicated process. The damage caused during sample taking, however, may be repaired and corrected during subsequent treatment. In the interest of providing sufficient information these examinations are always worth carrying out. As for the base metal, the results of spot analyses, which were arrived at by applying the methods discussed above, practically coincided with those of the corrosion products.

3.7.2. Spectrographic examination

The samples chosen were examined by a research worker at the Metallurgical Research Institute. For the evaluation of the metallographic examinations one had to know the exact composition of the base metal. The qualitative composition of the alloy as well as the relative quantitative distribution of the components were determined by laser-microspectrographic analysis at the Department of Analytical Chemistry, Veszprém University.

The appliance was operated by a Zeiss LMA-1 type controlled laser inductor and used an auxiliary spark discharge, while the spectrogram was taken by a Zeiss PGS-2 type spectrograph. The analytical provided the following information on the estimated quantities:

Base metal: Cu
1-10 % composition elements: Pb, Zn, Sn
Elements found in traces: Ag, Sb, Bi, Au
In some places near the surface: Fe, Ni

Tin is present as a composition element at the 1-2 % level. Lead content is higher than that and the presence of Zn in the amount of more than 1 % is surprising.

The traces of silver could have come from external silver plating, but it was established beforehand that there was no metal coating to be found. In this case it may be present as an accompanying substance of lead. The presence of gold may be accidental, too.

Antimony and bismuth could be the accompanying elements of the ores used for alloying and are often found in ancient bronze finds.

3.7.3. Metallographic examination

This analysis was carried out by the research worker of the Metallurgical Research Institute, a more detailed description including diagrams /2-9/ are included in Note 2. According to the scientist's conclusions the substance of the metal objects may be perceived as ternary bronze. Today bronzes of this sort are called red alloys[7]. Their plasticity, corrosion behaviour and strength characteristics are more favourable than those of binary systems. Accordingly, this kind of bronze can be treated as a ternary alloy. Its structure has to be analyzed and evaluated on the basis of the Cu-Sn alloy system keeping in mind that Zn and Pb were added purposely in order to decrease the area of the solid solution and thereby bringing about more favourably castability[8]. Of course, in ancient times this intentional application must be understood as an attempt to use appropriate mixtures of ores

whose qualities were recognized experientially in due course.

After it is cast, a solid solution or crystallites are formed in the structure of the cooled substance, while at the grain boundaries eutectoids take shape. In our case a relatively high lead content was found. Lead, however, forms a typically monotectic alloy-system with copper and therefore it is lead that will get separated at the grain boundaries. In those instances, therefore, where excessive rigidity is harmful for the cast substance, its properties are improved by additional alloying elements. The function of lead as an additive is to make the metal more workable and at the same time selflubricating. Since lead will not mix with the alloy but will be distributed evenly in drops or become enriched at the boundaries of the eutectoid, the resulting harmful side effect is that these lead drops constitute the weak points of the bronze object[9]. Harnesses are exposed to greater stress which justifies the application of this alloy for the making of the Roman objects examined.
For our purposes, the advantage of high lead content is that it brought about an even layer of $PbCO_3$ on the surface. Owing to the soil conditions /there were very low levels of chlorides/ this coating could function as a protective layer and since it is relatively stable, it could also reduce the rate of corrosion considerably. Most of the objects are, therefore, in a relatively good condition with an even lead carbonate layer on their surface which can be polished after treatment making them pleasing objects for the eye.

The above survey of the analytical results confirms repeatedly that examinations performed after the posing of relevant questions and carried out by external researchers will provide extremely useful information concerning the manufacturing process of the objects and the methods of treatment to be applied.

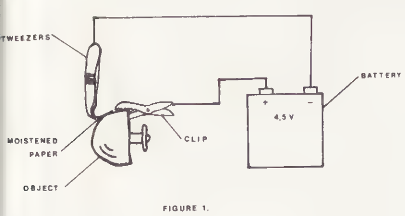
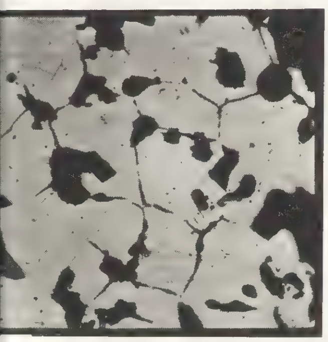
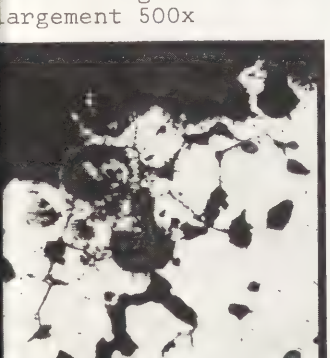


FIGURE 1.

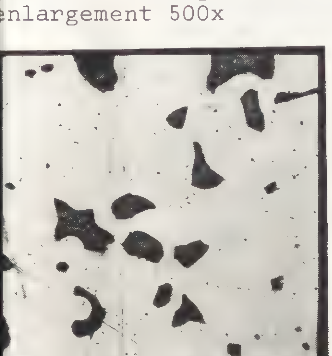
Fig.1. Analysis of the surface by microelectrolysis /After M.Laver[6] p.4.fig.1./



ig.2.Metallographical micrograph of sample Nr.1., without etching. Scale of enlargement 500x



ig.3. Metallographical micrograph of sample Nr.1., without etching. Scale of enlargement 500x



ig.4. Metallographical micrograph of sample Nr.1., without etching. Scale of enlargement 500x

4. Notes

4.1. Description of the spot-tests

4.1.1. Detection of lead on the surface of the object: a small piece of filter paper is impregnated with 2.8 pH buffer, the surplus is shaken off, pressed on the surface, than fresh /max. 1-2 days old/ Na-rhodizonate solution is dropped on the filter. In case of lead traces, lilac-pink colouring can be observed. Apart from lead, this reaction is given by Ag^{+}, Cd^{++}, Sh^{++}, but their sensitivity is much inferior to that of the lead ions /e.g. the rate of detection, compared to that of silver, is 1:5000/ /Feigl[5] p.437. 12/

4.1.2. Detection of iron by the help of dipyridyle paper /Feigl[5] p.161/: a stripe of filter paper is impregnated with 2 % α,α'-dipyridyle solved in alcohol, then dried. If a drop of the solution to be analysed is applied to it, we get a colouring from pink to red, depending on the iron content. The analysis can be performed on the surface of objects as well, according to the sketch on Fig.1.[6] Before analysis a few drops of a saturated solution of NaCl are placed on the test paper, pressed on the surface, and when the contact is good, the above mentioned colours will appear if iron is present. Reaction should be confined to a small area!

4.1.3. Detection of tin, based on the microelectrolysis method of M.Laver[6]: stripes of filter paper are impregnated with 5 % phosphomolybdic acid /Feigl[5] p.1o8/, placed into vapour of NH_4OH for a short while, then kept, after drying, in a dark, tightly closed glass jar. From the filter paper prepared this way, a small piece is cut, onto which a few drops of a saturated solution of NaCl are placed, this is then placed on the surface of the object according to the scheme shown in Fig.1. If a good contact is achieved, in a few seconds a deep blue colour will appear on the test paper in the presence of tin.

4.2. Metallographic analysis:
The samples submitted for analysis were embedded in the routine way, and polished smooth. After examination of the polished surface, the pieces were etched and observations repeated.
Evaluation of the micrographs:

4.2.1. /fig. 2./ Nr.1. polished surface of one sample, without etching, scale of enlargment 5oox. Close to surface, corrosion process started at the grain boundaries. Second phase, the δ-eutectoid is corroded as well.

4.2.2. /fig.3./ Another field on the previous /Nr.1./ sample, without etching, scale of enlargement 500x, the surface is corrode progressively towards the inner parts of the metal, corrosion type intercrystalline, corresponding to the previous type.

4.2.3. /fig.4./ Surface of the previous /Nr.1./ sample towards the inner metallic body, without etching, scale of enlargement 5oox, basic structure; solid solution / α - phase/, as a second phase, there is the δ - eutectoid of the grain boundaries.

4.2.4. /fig.5./ Another sample /Nr.2./, without etching, scale of enlargment 5oox, almost completely corroded, with very few intact metal inclusions. The structure of the corrosion product follows the original structure.

4.2.5. /fig.6./ Surface of the previous /Nr.2./ sample: lower laye without etching, scale of enlargement 500x, the thickening of the corrosion zone is apparent, the remaining metallic part is the α - phase solid solution /white/.
/The lead concentrated along the grain boundaries is also corroded

4.2.6. /fig.7./ Surface of sample Nr.3., without etching, scale of enlargement 500x; the second phase appearing in the α - solid solution is visible, that is, the δ - eutectoid, with the concentration of lead along its borders, present in the form of sharp lines. Failures characteristic of ancient melted bronzes are also present /dark pores/.

4.2.7. /Fig.8./ The micrograph shows the state of sample Nr.3. after etching. Scale of enlargement 500x, the dark parts are corroded grain boundary areas, the white spots are the intact meta with different concentration zones /inclusions and pores/.

4.2.8. /Fig. 9./ The micrograph shows the state of sample Nr.3. after etching, in a scale of enlargment bigger, than the previous ones /12oox/. The result is similar. The dark parts represent the α - solid solution, bordered by concentrations of lead. The light parts are the δ - eutectoid, details of the second phase.

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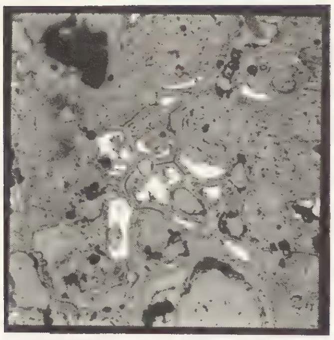
Fig.5. Metallographical micrograph of sample Nr.2., without etching. Scale of enlargement 500x


Fig.6. Metallographical micrograph of sample Nr.2., without etching.Scale of enlargement 500x

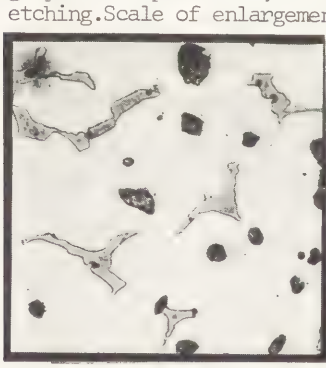
Fig.7. Metallographical micrograph of sample Nr.3., without etching. Scale of enlargement 500x

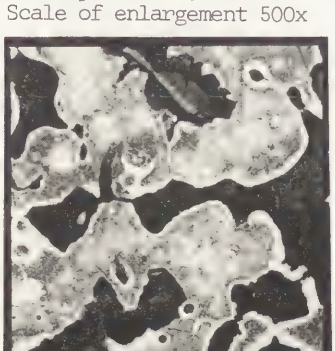
Fig.8. Metallographical micrograph of sample Nr.3., etched. Scale of enlargement 500x

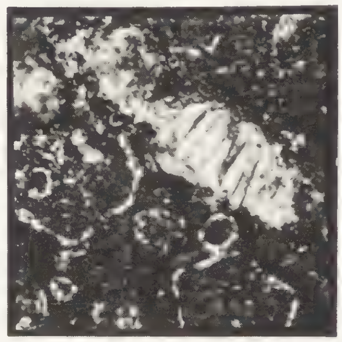
Fig.9. Metallographical micrograph of sample Nr.3., etched. Scale of enlargement 1200x

SUMMARY

The 15th C. párta and párta-belt to be discussed in the study were unearthed during the uncovering of the mediaeval cemetery at Sály in 1985. When lifting it up at the excavation site the párta was conserved on the skull by a solution of poly-vinyl-butyral in denaturated alcohol; the belt was stored in wet cotton wool and thymol disinfectant until restoration began.

The metal parts of the párta and the belt were cleaned by sodium hexa-meta-phosphate and Selekton B2 solution, conservation was carried out by Paraloid B 72 solution. For completions Viapal H210B5 was used, grossly incomplete fragments were mounted on duplicates. For the cleaning and conservation of the leather belt fat liquor was applied, a final treatment was carried out with sheepskin dyed with aniline.

RESTORATION OF A MEDIAEVAL PÁRTA[x] AND PÁRTA-BELT

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1. Introduction

The párta and the párta-belt to be treated in the study were discovered while unearthing the mediaeval graveyard at Sály in 1985. The párta was found in Grave No. 84/26, and the párta-belt in grave 84/8. The excavations were directed by Dr Károly Mesterházy. The objects are in the possession of the Hungarian National Museum.

1.1. Historical survey

The párta is the greatest ornament of Hungarian female headwear and is in fact closely related to the crown and coronet /diadem/. The crown has always involved the notion of saintliness and virginity. It may not be accidental that lily motifs are often found on crowns, that there are lilyornamented, plated pártas and that this type of headgear was and has remained the typical attire of young maidens.

The wearing of pártas can be observed as far back as the Hunnish period. The custom of wearing them may be termed as basically unbroken from the 10th 6. onwards.

In the 15th C. helical pártas appeared. The párta chaplet was plaited from rushes, covered by fabric and velvet or silk on which the helical decorations, beads and "glitters", i.e. the small, shiny metal flitters were sewn. From among the material remains of female attire it is usually these pártas that survive most intact since the textiles are held together by the metal and glass fittings and are conserved by the metallic salts.

It is better to conserve them in situ after which they can be lifted and stored. The condition of the finds is influenced by the soil of the area where the cemetery is situated as well as the disintegration process of the dead body; this accounts for the fact that in one and the same cemetery in one grave the párta has remained almost completely intact, while in another only the metal decorations could be saved.

The soil conditions of the Sály cemetery were likewise varied and thus the párta to be discovered here was found in a relatively good condition, while from the neighbouring grave only fragments of the helical decoration could be recovered. For conservation in situ only materials which are easy to remove later on during restoration are to be used.

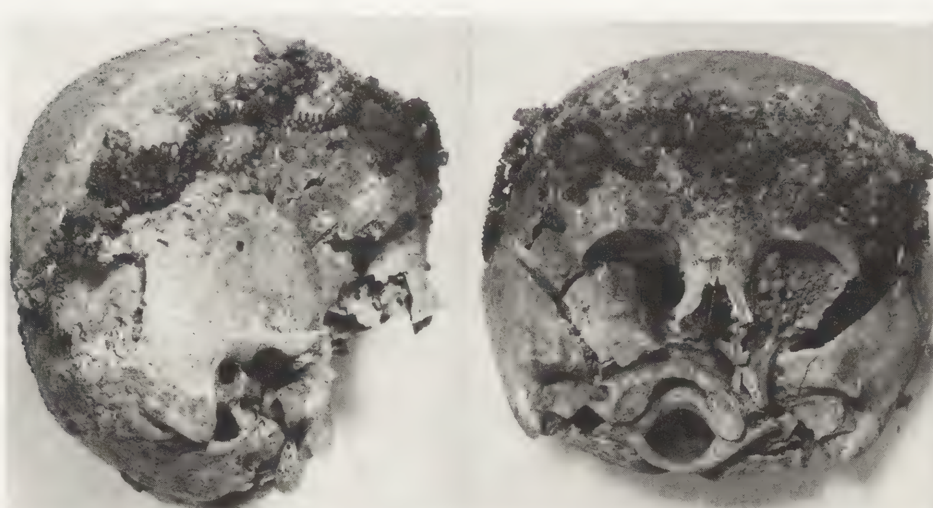

Fig. 1-2: The párta after lifting at the excavation site

x párta: /Hungarian/ girl's headdress

2. Párta

2.1. Description, conservation and restoration

When lifting at the site, the párta was conserved on the skull by a thick solution of polyvinyl-butyral in denaturated alcohol whic was later carefully dissolved and removed by denaturated alcohol from the skull. /Fig.1-2/

The full length of the párta spiral is 31.7 cm. 9 glass beads, 1 round flitters /diameter:0.8 cm/ and 7 hanging spangles /length: 0.9 cm/ turned up as well. The spiral was made of 0.35 mm copper wire, the flitters from 0.05 mm thick copper plates.

The spiral was soaked in 5 % hexametaphosphate for 1 day and then brushed over by a fine copper brush. It was cleaned in 2 % Evatri Selekton B_2, rinsed in distilled water several times and finally dried. It was cleaned once again with a bottle brush, coated by Schlippe salt solution and conserved by a 5 % solution of Paraloi B72 in acetone-toluene /1:9/.

The weak and very thin flitters were taken up by sticking them onto Japanese vellum with a thick solution of PVB. Afterwards the were placed in 5 % Evatriol Selekton B2 solution. After cleaning the flitters were dissolved from the Japanese tissue, soaked in distilled water, dried and conserved as described above. Since th condition of the small metal plates made it impossible to complet them by filling the gaps, the flitters were stuck onto 0.05 mm thick copper plates which were cut to shape and patinated with Schlippe salt beforehand. For attachment a thick solution of Synocryl 9122 (poly-butyl-methacrylate/ in toluene-acetone was use used.
The trimmings of the párta were originally attached to a textile base as was concluded from the remains comprising several mm^2 and found when the headwear was removed from the skull. Since we did not succeed in identifying the original fibre, the restored metal decorations were fixed onto a piece of plain weave textile lined by thin felt. The arrangement of the spiral and the flitters with a hole in their middle was unambiguous, while the position of the suspended spangles and beads could not be established firmly. Therefore from among the various possible arrangements one was chosen for the reconstructed version. /Fig. 3-4/

There were two ways for the fastening of the párta onto the head: the headwear was either long enough to embrace the skull and was then held together by a hook, or it did not go round and was fastened by ribbons.

The headdress in question probably comes under the second type as is suggested by its length and the fact that no hook was found.

Analogies for the reconstruction of the párta were found in the mediaeval excavation material from Csut, Csecstó and Kaszaper /se references/.

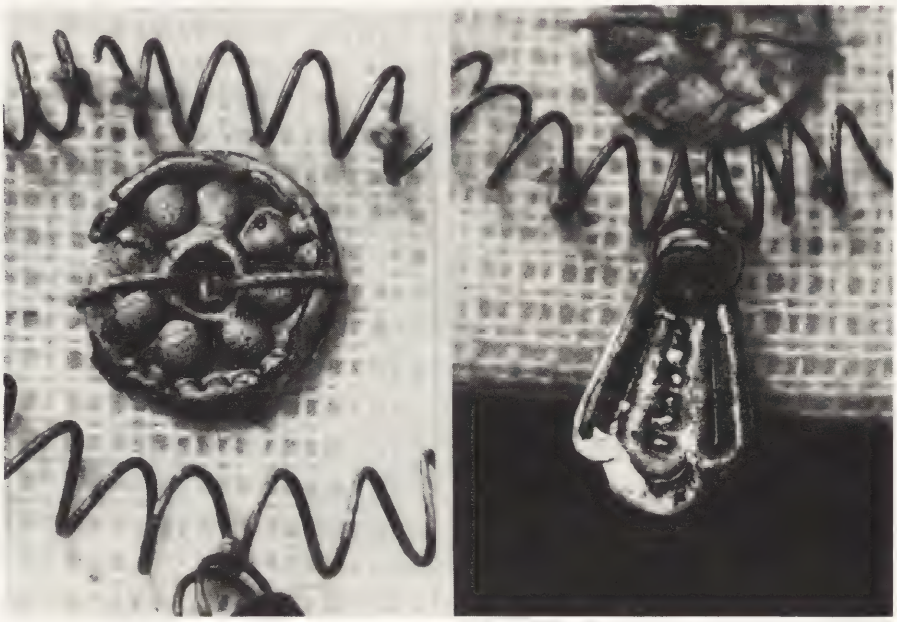

Fig. 3-4: Details of the finished párta

3. Párta-belt

3.1. Historical review

Belts were one of the most important pieces of clothing in the life of oriental nomadic tribes. In Europe the custom of using belts was spread by the oriental peoples of the migration period.

The various types of mediaeval ornamental belts began to appear from the 10th C. onwards. Their decoration was related to the goldsmith's craft of the age. The most richly decorated parts are the buckle and the belt-end. In the 13th C. the wearing of studded belts could not have been widespread since they are not found in ordinary graves.

From the 14th C. onwards belts became more popular. A liking for splendour of the less well-to-do middle classes is displayed by the wearing of párta - belts.

The more sophisticated, chiselled and punched belt ornaments made of precious metals and decorated by vegetal, figural or geometrical ornamentation constituted part of the aristocracy's jewellery. The belt was included in the last will, it could be taken as security to cover a loan and functioned almost as a means of payment. In this time it was worn in the pelvic area.

In the 15th C. it was worn around the waist and served a practical purpose. There were pin-cases, bunches of keys and cosmetics hanging down from it; on belts for men bags and daggers were hung. The belts were often covered by textile. Textile remains were discovered on the belt-end of the find from Sály as well. Belts were worn by men and women alike, but it constituted a piece of children's garments in the first place.

3.2. Description of the párta-belt

After lifting the belt was packed in wet cotton wool with a couple of pieces of thymol placed next to it for disinfection. It was taken to the restoration workshop within a few days.

The full length of the recovered leather remains is 49.2 cm. On the 1.7-centimetre wide belt there were 8 mountings /1.5x1.5 cm/ and 1 case holder /4.6x1.3 cm/ attached by 4 rivets, also found /Fig.5/.

The square-shaped mountings were made from a bronze sheet by pressing. They are decorated by 4 interlocking, stylized lilies, a typical ornamentation of the late Gothic period. The pierced appearance of the areas in between the lilies was achieved by punching the originally unbroken surface from above. Piercing of this sort also shows that the mountings were originally made from a very thin material. The centre of each mounting was pinned through by a rivet which also served to fix them to the belt. The distance of the mountings from each other is 0.3-0.7 cm. These studdings were always found to have decorated children's belts except for two cases, where they occurred as decorations of adult pártas. On the case holders there are rows of Gothic "I" minuscules. These can be religious inscriptions turned into ornamentation or some other pattern originating from the word "Jesus".* On one of the rivets of the case holder a small, slightly bulging, round--shaped bronze plate was found which may have been an under-plate when the rivet-end was flattened.

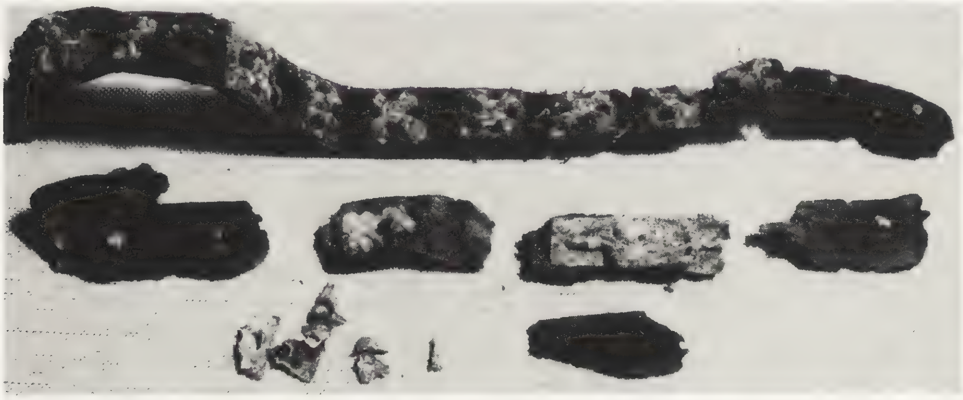

Fig.5: The párta-belt after lifting at the excavation site

* The former interpretation was given by Magda B. Oberschall, the latter by Győző J. Szabó

Fig.6: Detail of the completed leather belt

3.3. Cleaning, conservation and restoration of the leather

The remains of the belt which were made of sheepskin and tanned b some vegetable matter were soaked in a 5 % solution of concentrated Evamin in distilled water. The pieces were blotted i between filter-paper and then placed into a mixture of glycerine /50-50 %/ for 2 days. Finally the fragments were put into fat liquor for 24 hours. /Fat liquor: 150 g fatty alcohol sulphate, 50 g lanoline, 100 g hoof-oil, 3 g thymol dissolved in alcohol, added to 1 litre warm distilled water./

After cleaning and conservation the leather fragments were presse and dried in between filter-paper.

Since the leather survived in a relatively good condition and the aim was to leave both sides visible, sheepskin thinned down to th appropriate size and dyed a matching colour was placed between th grain and flesh side of the original leather. The new leather was stuck to the original by transparent Elastosil E 41 adhesive. Thi substance was chosen because it is flexible and strong, it can be dissolved after some time for future removal and does not leave behind stiff spots on the leather. The leather was dyed using: 30 ml ammonium sulphate and aniline dye in 1 litre of a solution of 7 dl denaturated alcohol + 3 dl distilled water. For tobacco brown a mixture of 1 part blue, 2 parts of lemon yellow and 2 parts of direct brown was prepared. The dyestuff was rubbed into the leather by a cotton wool wad /Fig.6./.

3.4. Cleaning, conservation and completion of the mountings

After soaking the mountings in a 10 % solution of hexametaphospha they were cleaned in a 5 % solution of Selekton B2. The quality o the mountings did not permit the application of more powerful compounds or vigorous mechanical cleaning, thus after thorough cleaning by the compounds mentioned above the reverse sides were coated by a thin layer of Viapal H 210 BS synthetic resin. The resulting firmness made it possible for us to clean the faces of the mountings with a 15 % warm solution of Selekton B2 down to th metal. Completions and missing parts were made from Viapal dyed with Diamant powder metal and earth colour. Grossly incomplete mountings were not completed, the fragments were mounted on a duplicate instead.

Using silicone negatives taken from the original as many copies o mountings were made as determined by the number of holes on the belt. The mountings prepared in this manner as well as the case holders were then stuck on the belt by Elastosil E 41.

Since there was no belt-end or buckle recovered from the grave, a buckle and belt-end originating from another grave were attached to a piece of leather of optional size indicating that the end parts of the restored belt could have been similar.

Part of the cast bronze belt-buckle is the double belt-fastener plate decorated by a row of hearts; it can be attached to the bel by two rivets. The tongue of the buckle is bronze wire. The size of the buckle frame is 2x1.7 cm, that of the belt fastener 4.2cmx 1.2 cm.

Analogies for the reconstruction of the párta- belt were provided by Kálmán Szabó's excavations in the Great Hungarian Plain, the remains of mediaeval cemeteries at Csut and Mohács-Csele-patak as well as the finds from Kaszaper, Zagyvapálfalva, Zuh, Tiszaörmény Sárospatak and the earlier excavated finds at Sály /see bibliography/.

The fact that both the belt fittings and the glitters decorating the párta were of low quality and seem to have been used widely proves that they may have been cheap, mass-produced articles within the reach of the more well-to-do middle classes. /Fig.7./

Substances applied:

Polyvinyl-butyrale /PVB/
Synocryl 9122: polybutyl-methacrylate
Evatriol: anionic detergent
Selekton B_2:ethylene-diamine-tetra acetic acid, complex forming
Schlippe salt: sodium-thio-antimonate
Paraloid B72: methyl-acrylate ethyl-methacrylate copolymer
Thymol: methyl-isopropyl phenol $C_{10}H_{14}O$
Evamin CC: non-ionic detergent
Viapal H210BS: polyster resin

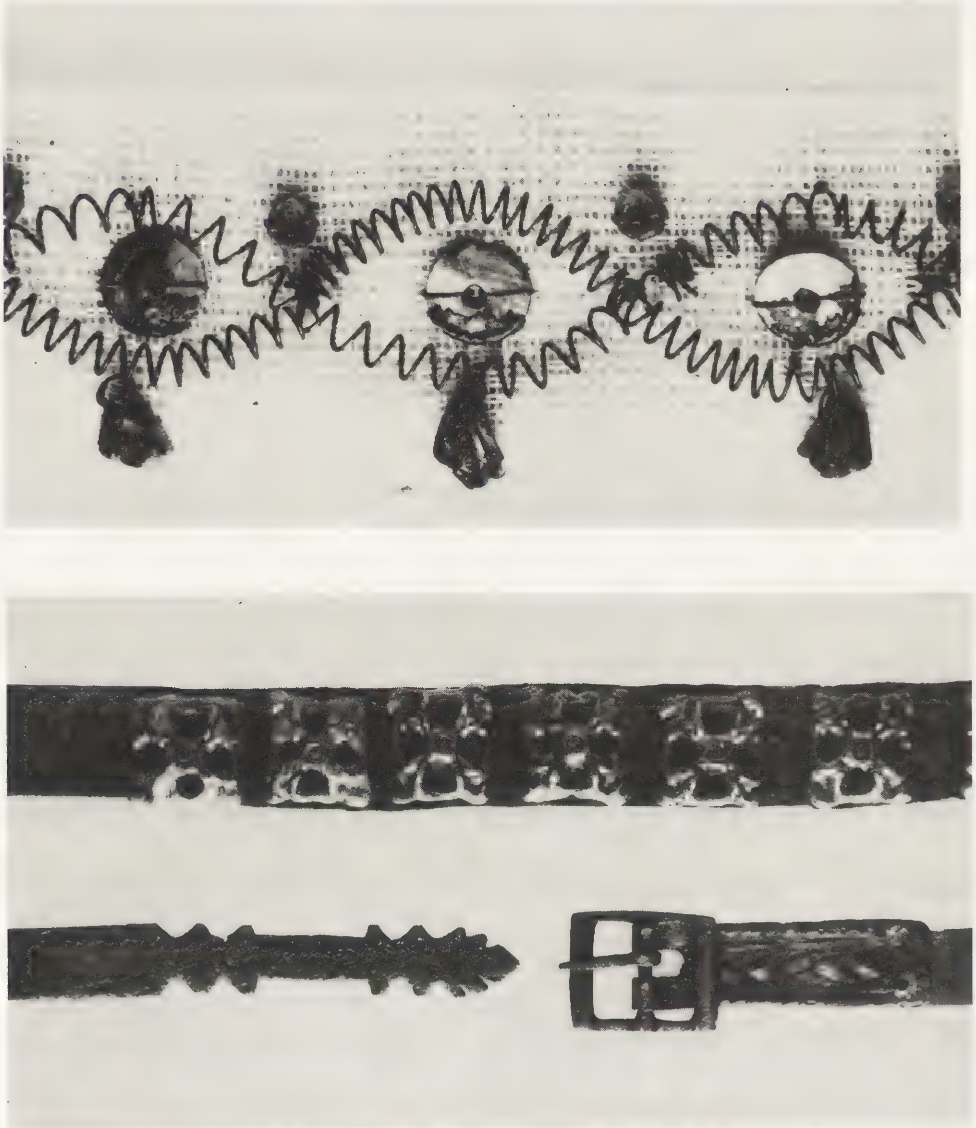

Fig.7: The párta and the belt after restoration

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STABILIZATION OF CORRODED COPPER ALLOYS : A STUDY OF CORROSION AND DESALINATION MECHANISMS

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SUMMARY

A study of more than 12,000 objects recovered from maritime and terrestrial archaeological sites has shown that there are several parameters that determine the rate of release of chloride ions during conservation treatment. Factors such as metallographic structure, salinity and dissolved oxygen levels during burial, give rise to a series of characteristic chloride release rates that enable treatment times to be calculated. The data relates principally to desalination in deionized water and sodium sesquicarbonate solutions and secondly, to sodium dithionite solutions.[1] The results show that stabilization of badly corroded objects can be achieved through extended washing programmes. The physical basis for such treatments is described in terms of a model that also permits calculations on the apparent depth of corrosion.

Introduction

In an ideal situation a conservator has ample opportunity to properly assess what type of treatment is needed to stabilize a corroded object made of copper, brass or bronze. Factors that influence the choice are the presence or absence of 'Bronze Disease' and what changes in patination (if any) are acceptable. The decision also depends on the composition of the parent alloy and on the lead time before the object is to be returned for display or further examination. Ways of overcoming some of the problems associated with the choice of treatments have recently been reported[1] and this paper will address the area of predicting how long the overall treatment takes, and how to cope without the aid of sophisticated monitoring equipment.

The conservation of more than 12,000 copper-based artefacts over the past eight years forms the database from which the mechanisms controlling the rate of desalination have been deduced. Because the variability of the extent of corrosion within an individual archaeological site can be quite marked, it was necessary to collect information from a number of locations in order to maximise the reproducibility of results. Most of the objects examined have come from ten shipwreck sites off the West Australian coast which date from the *Batavia* (1629) to the *Macedon* (1883). The warm tropical to sub-tropical waters[2] range in temperature from mean annual values of 17° to 25°C and the sites are generally well oxygenated. These conditions favour extensive corrosion of metals. Coinage recovered from Graeco-Roman land sites has also been examined and the results are essentially the same as those found for objects recovered from the sea.

Inspection of objects previously treated in the W.A. Museum's laboratories had shown that many of the bronzes were subject to further corrosion under storage in ambient conditions, 20±4°C and 55±15% relative humidity. The objects had been given 'short' treatments of a few weeks duration and this was manifestly insufficient to effect stabilization of extensively corroded materials. It was decided to carry out a series of extended washing regimes to effect stabilization of the objects. In order to ascertain when chloride removal had been "completed" the wash solutions were regularly monitored for chloride and copper ions. Periodic determinations of the concentration of lead, tin and zinc in the washes were also made. The importance of monitoring treatment solutions has previously been demonstrated.[3] Corrosion reactions, particularly those involving brasses, can take place without there being any readily apparent change in the degraded object. A detailed analysis of the rates at which chloride ions are released into deionized water and sesquicarbonate solutions has established the basis of a physical model which adequately explains why the treatments are diffusion controlled. The time taken to remove the available chloride from the object is also reported and it is dependent on the composition of the parent alloy and the microenvironment from which the object was excavated.

Results and Discussion: Model for chloride removal

Most of the treatments investigated in this programme were based on desalination in deionized (distilled) water or in sodium sesquicarbonate solutions because of their minimal effect on patination and because they are still the most commonly adopted methods. The results of this work are therefore of major relevance to the majority of objects conservators.

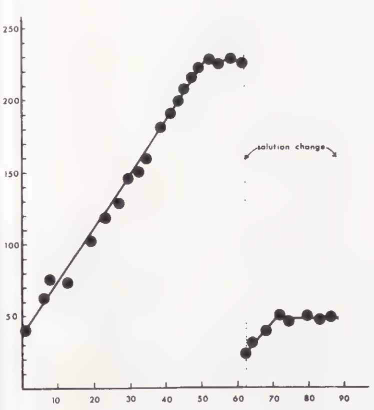

Fig. 1: Plot of chloride ion concentration versus the square root of treatment time ($hr^{\frac{1}{2}}$) for two bronze door pins from the *Batavia* (1629) in 80 ℓ of 2 wt% sodium sesquicarbonate. The composition of the bronze is given in Table 1.

The basic behaviour of archaeological copper alloy objects is clearly demonstrated by two bronze door pintles from the *Batavia* (1629) which were treated by the traditional "strip" in 10 wt% citric acid (2 wt% thiourea) for two weeks and then washed in 2 wt% sodium sesquicarbonate for 40 weeks. Two other *Batavia* door pintles had been previously treated by the same method but without the extended washing and they had subsequently showed signs of extensive corrosion despite their coating of Incralac. The chloride release data is conveniently displayed as a function of concentration and the square root of treatment time. Inspection of the graph (Figure 1) shows that the chloride concentration increases monotonically until a plateau is reached and, once the solution is changed, the chlorides are released at a slower rate until a second and lower plateau is obtained. If necessary, further solution changes can be made and the process repeated until no more chlorides report to the wash solution. The cause of the extensive corrosion of these bronze fittings is partly due to the high level of iron impurities (2.1 wt%). A discussion on the long-term corrosion effects of such impurities has previously been reported.[4]

The chloride release rates, based on the linearly increasing sections of the graph, are 3.73±0.15 ppm.$hr^{-\frac{1}{2}}$ and 2.49±0.81 ppm.$hr^{-\frac{1}{2}}$ for the first and second washes respectively. The scatter of the data is due to errors associated with sampling (insufficient mixing of the 80 litres of wash solution) and with

chloride determinations using a Buchler-Cotlove chloridometer. The data was analysed using a linear regression programme on a Texas Instruments (TI-55) calculator.

The bronze door pintles were given further washing in 1 wt% sesquicarbonate solutions for an extra 234 days to see if significant amounts of chloride remained behind after a total period of 280 days in the 2 wt% solutions. A total of 30 grams of chloride (0.07 wt% of the original mass) was removed during the sesquicarbonate washing and of this, some 65% came out in the first wash and a further 15% in the second wash. The treated pintles show no signs of corrosion after four years in ambient storage conditions which shows that the extended washing will stabilize extensively corroded objects with minimal changes to their patination.

Small differences in the basic behaviour outlined above will occur if secondary corrosion products or other materials precipitate on the surface of the object and effectively hinder the outward diffusion of chloride ions. Precipitation from sesquicarbonate solutions of the deep blue crystals of chalconatronite $Na_2Cu(CO_3)_2 \cdot 3H_2O$, can slow down the release of chloride ions. Occasionally unusual corrosion products can form on objects during extended washing, e.g. a film incorporating Na_3BiO_4 was found on the surface of the *Batavia* bronze door pins, but these films are often readily removed by chemical stripping or careful brushing.

The fact that hundreds of objects give the same type of response as shown by the bronze door pintles from the *Batavia* indicates that common phenomena control the removal of chloride ions. One common factor is that all the copper brass and bronze objects have an adherent and relatively dense cuprous oxide layer (Cu_2O) on their surface adjacent to the corroded metal. The outer blue-green layers of copper (II) hydroxychlorides such as paratacamite ($\gamma Cu_2(OH)_3Cl$) have much lower densities, 3.75 $g.cm^{-3}$ c.f. 6.06 $g.cm^{-3}$ for Cu_2O[5], and will not be rate determining.

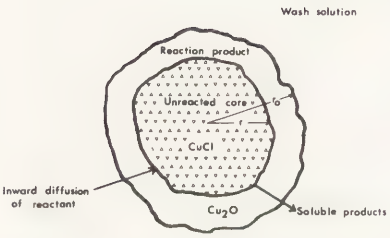

Fig. 2: Schematic cross-section through a corroded metal artefact with diffusion through the remnant structure, or products of reaction, as the rate controlling step.

The long reaction periods of six months or more to remove the chloride ions are somewhat akin to the slow reactions associated with heap leaching of copper from mineral dumps[6] where there is slow ingress of reacting solutions, through a reaction product layer, into low grade ores in which the copper mineral is dispersed. For corroded copper alloys we can equate the reaction product layer in the leached mineral with the cuprite (Cu_2O) film and the unreacted low grade ore as the chloride containing corrosion products disseminated within the residual metal structure. The model assumes that the reacting species (copper (I) chlorides) are evenly dispersed through spherical grains of the host matrix, which is the corroded metal artefact. A cross-section of the model is shown in Figure 2 where r_o is the radius of the unleached (untreated) object and r is the radius at the reaction boundary, which moves inwardly as the washing proceeds. The kinetics are controlled partly by the rate of transport through the chloride depleted (reacted) layer which lies between the reacting front and the outer regions, and by the rate of reaction within the reaction zone. If the major hydrolysis product in the corroded metal zone is cuprite then there will still be 'gaps' left for the chlorides to diffuse through since reactions such as

$$2CuCl + 2OH^- \rightarrow Cu_2O + 2Cl^- + H_2O \qquad (1)$$

will leave the intergranular or interdendritic space more open since although nantokite (CuCl) has a similar volume of 23.9 cm^3 to cuprite (Cu_2O) at 23.65 cm^3, the stoichiometry of equation 1 shows that the void space would be increased if such reactions occurred. A combination of oxidation and hydrolysis of copper (I) chlorides, could result in dissolution of the corrosion products, as shown in equation 2

$$4CuCl + O_2 + 8HCO_3^- \rightarrow 4Cu(CO_3)_2^{-2} + 4H^+ + 4Cl^- + 2H_2O \qquad (2)$$

If the remnant structure or products of the hydrolysis occupy roughly the same volume as was dissolved during the chloride removal, then a special solution can be obtained[7] where the total flux is given by

$$\frac{dn}{dr} = 4\pi r^2 D \frac{dc}{dr} \qquad (3)$$

where n is the number of moles of chloride, r is the radius of the reacting front (see Figure 2), D the diffusion coefficient and c the surface concretion. The washing experiment approximates to steady state conditions in which the rate of diffusion through the pores in the shell outside the reaction zone equals the rate within the reaction zone. Under these conditions there will be a constant flux of materials across the values of r between r and r_o which changes equation 3, upon integration, to the form where the rate of increase in the number of moles of chloride, $\frac{dn}{dt}$, is given by the expression

$$\frac{dn}{dt} = \frac{-4\ DCr.r_o}{(r_o - r)} \qquad (4)$$

under the boundary conditions that c, the reaction surface concentration is small compared with C, the bulk concentration of reactant. The rate at which the reaction front radius changes is given by

$$\frac{dr}{dt} = -\frac{v\ DCr_o}{r(r_o - r)} \tag{5}$$

where v is the molar volume of the reacting (mineral) species. The above expression can be formulated in terms of α, the fraction of the reaction completed the time t, to give

$$\frac{d\alpha}{dt} = \frac{3vDC}{r_o^2}\ \frac{(1-\alpha)^{1/3}}{[1 - (1-\alpha)^{1/3}]} \tag{6}$$

which results in $1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = (2vDC/r_o^2)t$ (7)

for the condition that $\alpha = 0$ at $t = 0$

Thus a plot of the function $1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3}$ versus time should give a straight line with zero intercept and a slope of $(2vDC/r_o^2)$ if the model accurately describes the chloride removal process. Data from the first stage of the sesquicarbonate washing of the *Batavia* bronze pintles was used to test the model and the results are shown in Figure 3 for the first fifty days of the treatment. The relationship between the alpha function and time was given by

$$1 - \tfrac{2}{3}\alpha - (1-\alpha)^{2/3} = 0.0000803t + 0.00484 \tag{8}$$

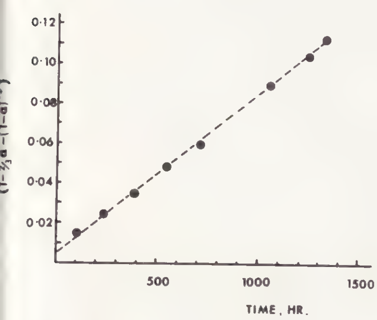

Fig. 3: Diffusion model correlation of data for chloride extraction from *Batavia* bronze door pins in 2 wt% sodium sesquicarbonate solutions at 23±2°C and pH of 10.0±0.1 .

which had a correlation coefficient for the least squares fit of 0.9993, where the time is in hours. The intercept value of 0.00484 is essentially zero, as expected, since there was no initial rapid increase in chloride. Non zero intercepts would be found in cases where there was surface chloride, e.g. when sea water had evaporated to dryness on the surface of the corroded fitting and rapidly dissolved as soon as the object was placed in the wash solution. The zero intercept also supports the observation that reactions of the type,

$$Cu_2(OH)_3Cl + 4CO_3^{2-} \rightarrow 2Cu(CO_3)_2^{2-} + 3OH^- + Cl^- \tag{9}$$

do not occur to any significant level in 1 wt% and 2 wt% sesquicarbonate solutions, viz., the blue-green patina is largely unaffected by the washing process. The value of the slope was $8.03 \times 10^{-5}hr^{-1}$ or $2.23 \times 10^{-8}\ sec^{-1}$ and can be used to calculate values of r_o, the radius of the 'untreated' artefact. If we assume that the reacting species is the hydroxide ion as shown in equation 1, then at pH 10.0,C will be 1×10^{-4} M, V, the molar volume of CuCl is 23.9 cm^3 and D, the diffusion coefficient of the reacting ion through the Cu_2O layer is approximately $5 \times 10^{-6}\ cm^2.sec^{-1}$,[8] then r_o will have a value of 1.03 cm. Such a value for r_o implies that the reaction zone, the area with copper (I) chlorides dispersed through it, is 1 cm deep into the object which is entirely consistent with the observed corrosion phenomena. Although the bronze sampled for chemical analysis was apparently solid and was predrilled to a depth of 5 mm prior to the core sample being taken, the total metal content (copper, tin, lead, zinc, etc. as shown in Table I) amounted to only 98.24% which is consistent with significant mineralization at the depth range 5-10 mm. Further evidence of the depth of chloride penetration into bronze artefacts was seen when a section was cut through a corroded leaded brass pintle pin from the wreck of the *Cumberland* (1830) and was left exposed in the laboratory for three weeks. A series of concentric corrosion spots appeared approximately 1.5 cm in from the former sea water-metal interface. Active 'Bronze Disease' broke out on the polished section from the tip of the pin (see Figure 4) which was 0.5 cm into the object. Despite outward appearances of a relatively sound casting, there were many defects such as casting porosity in the centre of the pin and chloride ions had penetrated several cm into the metal structure over a period of 155 years in fully oxygenated sea water at 18.5±4.6°C.[2]

Fig. 4: Metallographic transverse section of leaded brass rudder pintle pin from *Cumberland* (1830) showing active corrosion. The surface of the section was 5 mm from the tip of the pin. The analysis of the pin is shown in Table 1. Full width of image 5.58mm.

Detailed analysis of the rate of chloride release from a series of aerobically corroded copper, brass, and bronze objects and one cathodically protected bronze swivel cannon from the *Zuytdorp* (1712) all conformed to the relationship that

$$1 - \tfrac{2}{3}\alpha - (1-\alpha)^{2/3} = \left(\frac{2vDC}{r_o^2}\right) t$$

with the mean value of the slope being $(153\pm70) \times 10^{-6}\ hr^{-1}$ which would give a mean r_o value of 7.4±3.4 mm which is consistent with typical values for depth of intergranular/interdendritic corrosion found in samples analysed metallographically, as shown in the polished section of a nail from the *Rapid* (see Figure 5) where intergranular corrosion has penetrated 7.3 mm.

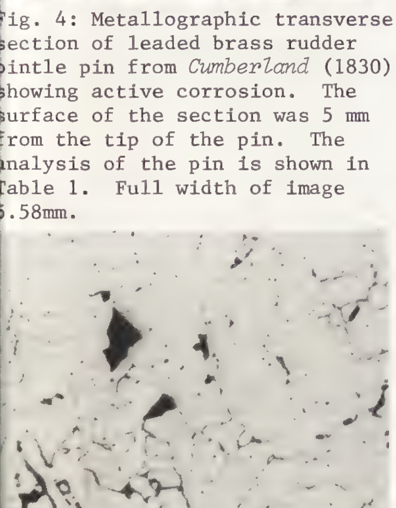

Fig. 5: Metallographic structure of a longitudinal section of the shank of a corroded brass nail from the *Rapid* (1811) after etching in 2 wt% alcoholic ferric chloride. The nail had been hot worked after casting. Full width of image 753 μm.

A dramatic example of the depth of corrosion penetration was seen during wet chemical analysis of some leaded bronze sheathing tacks from the *Lively* (c.1810).[1] In order to determine how much chloride was in the total mass of the nail, a number of sections were dissolved in 10 wt% nitric acid. Digestion of the samples resulted in hollow cores of creamy-white cassiterite (SnO_2) remaining in the acid solution (see Figure 6). Analysis showed that although some tin (IV) corrosion products dissolved, most of the matrix remained, whereas

Fig. 6: Residual structure of corroded leaded bronze sheathing tacks, *Lively* (c.1810), after digestion of tacks in warm 10 wt% nitric acid. The creamy-white solid was identified by XRD as cassiterite, SnO_2. The chemical composition of the tack is listed in Table 1. Full width of image 6.6mm.

the corroded copper rich phases and all the uncorroded core were dissolved in the warm acid solution. The total chloride content of the untreated nails was 1.18±0.37 wt% or 24 times the amount in the 'uncorroded' core.

Effects of composition and on-site microenvironment on chloride release rates

In order to understand why objects took different times to stabilize and why apparently similar alloys from the same wreck site had corroded in different ways, a systematic study of the effects of on-site microenvironment was made. A number of objects were sampled for wet chemical analysis[9], electron microprobe studies[10], corrosion products[11] and the associated concretions were also studied[12]. The results show that the corrosion of copper and its alloys with tin and zinc are dependent on factors such as salinity, temperature, dissolved oxygen and metallographic structure. Since the salinity of the Western Australian shipwreck sites were all in the range 37-35 ppt and the mean annual temperatures varied from 25.5 to 18.3°C,[2] the other factors of metal structure and on-site microenvironment were seen to be of major significance.

It has been shown that the corrosion mechanism[10,11,13] of bronzes changes with the depth of burial. If an object is lying proud on the seabed and in well oxygenated waters there is kinetically controlled oxidation of the copper rich α phase. This results in objects having an apparently sound structure and will give rise to a typical blue-green patina overlying the red-brown cuprous oxide layer. Bronzes that lie buried under several centimetres of sand corrode in a very different manner since the oxygen diminished environment results in selective corrosion of the tin rich phases, such as the $\alpha + \delta$ eutectoid. The corrosion mechanism is under thermodynamic rather than kinetic control. Objects recovered from these 'partly aerobic' conditions have a more open surface structure which is more friable and consists of a large amount of tin (IV) and some tin (II) corrosion products intermixed with Cu_2O and copper (II) hydroxy chlorides. If the objects have been buried in anaerobic conditions the corrosion products will be principally metal sulphides. The fourth type of microenvironment is found for objects that have been cathodically protected by galvanic action by a more reactive metal such as iron. Bronzes which are normally free of concretion are found to be covered with a thin (2-3 mm) calcareous layer that is hard and impervious. Once the concretion has been removed the objects appear to be in a sound condition and are normally covered with a Cu_2O or a mixed Cu_2S/Cu_2O patina.

Since we have shown that the diffusion controlled release of chlorides is largely dependent on the microstructure of the object and the copper (I) oxide layer on the surface, it is now possible to rationalize the data from more than 50 washing experiments. Plots of the raw experimental data give chloride release rates in parts per million per hour$^{\frac{1}{2}}$ (ppm hr$^{-\frac{1}{2}}$) simply because of the choice of analytical procedures used in the laboratory. A convenient way to minimise variations in apparent release rates is to correct for the solution volume and geometric surface area of the objects. The 'normalised' release rates are given by the formula

$$R_n = \frac{R_{ppm} \cdot x}{y} \tag{10}$$

where x is the solution volume in litres, y the surface area in square centimetres and R_{ppm} is the release rate in ppm.hr$^{-\frac{1}{2}}$. Normalised rates will have the units of mg.cm^{-2}.hr$^{-\frac{1}{2}}$. Since the data obtained is normally small fractions of a mg.cm^{-2}.hr$^{-\frac{1}{2}}$ it is reported for convenience in the units of μg.cm^{-2}.hr$^{-\frac{1}{2}}$.

Whilst it is realized that real surface areas will be considerably greater than those determined geometrically, the improvement in the quality of the data by using the former values would probably not justify the amount of work involved in such measurements.[14] Since each of the data sets relates to the treatment of many objects, the natural variations in release rates will tend to be averaged out. The mean values of the normalised release rates for copper, brass, bronze and composite objects recovered from different microenvironments are shown in Table 2. Inspection of the data shows that there are significant differences in the chloride release rates for the various alloys. Because of the limited on-site documentation of artefact microenvironment for some wreck sites, we are not able to further define the aerobic category into fully oxygenated and partly oxygenated. However, it is readily apparent that chloride ions are removed from aerobically corroded bronzes at a much greater rate than for brasses which in turn are faster than copper. Such trends reflect the differences in the way the metals corrode.

Copper degrades primarily through erosion and intergranular corrosion. The treated objects had copper contents of greater than 98%[9] and their metallographic structure consists of single phase α solid solution with various impurities and inclusions such as droplets of lead and particles of Cu_2O[4]. Brass objects generally had a single phase α brass structure[15] but some had enough zinc to give significant amounts of the zinc rich β phase. Many shipwreck brasses have been subject to dezincification[16] and selective corrosion of the zinc rich β phase. As the microstructure is "opened up" during corrosion, chloride ions will diffuse into the matrix and form relatively insoluble copper (I) chlorides which will be 'trapped' inside the

Cu_2O layers. Metallographic examination of shipwreck bronzes[10,15,17] has shown that they are often subject to selective corrosion of the tin rich phases such as the ($\alpha + \delta$) eutectoid. Electromicroprobe studies of sectioned metals shows that there are significant amounts of tin (IV) and zinc (II) corrosion products within the degraded structure. Since chloride ions are readily abundant in sea water it is not surprising to find that greater amounts of chloride had diffused into bronze and brass objects to 'balance' the Zn^{2+} and Sn^{4+} ions than into the single phase copper objects where the major corrosion products are copper (I) compounds. Typical values of the amount of chloride extracted during sesquicarbonate treatment are 0.064 wt% for bronze and brass and 0.026 wt% for copper. Objects having higher concentrations of chloride in them would be expected to release them at a faster rate. For example, materials such as iron and glass have higher release rates partly because they have a greater amount of chlorides in them. The amount of chloride in the untreated objects is in the order of 0.8 wt% or some twelve times the amount typically extracted from bronzes. Details of chloride and sulphate removal for glass and ceramics are reported elsewhere.[18] Because degraded glass does not have such a coherent diffusion barrier as the Cu_2O layer in copper and its alloys, chlorides will tend to diffuse out at a much greater rate than commonly found in aerobic washing regimes.

When copper corrodes in an anaerobic environment the corrosion products are dominated by copper sulphides which range from Cu_2S through $Cu_{1.93}S$ and $Cu_{1.8}S$ to CuS.[12] Chloride ions are present mainly as CuCl along grain boundaries. Although sulphides are present as corrosion products on bronze objects, they are mainly found in the outer corrosion layers with chlorides being found deeper within the metal structure. Objects that had been subject to cathodic protection from corroding adjacent iron components are included in this category since the microenvironment under the protective thin calcareous layer is essentially anaerobic.[12] The release rates found for objects recovered from anaerobic conditions can be rationalized in the same way as was used for the aerobic data.

Prediction of treatment times

Using the information outlined in the preceding section, it is now possible to predict with reasonable confidence how fast chloride ions will be released from corroded copper alloys when they are first placed into sesquicarbonate wash solutions. It is of major importance for those concerned with laboratory management to know how long an overall treatment will take so that appropriate budgeting of resources and charges for clients can be made. If an object is suddenly required for display, a conservator needs to have guidelines by which one can gauge whether or not it is safe to temporarily interrupt the treatment.

In an attempt to see if there were any systematic trends in the amount of chloride released at each stage of the stabilization process, the concentrations at which plateaus occurred were noted and the results indicated that there was no apparent order. By comparing the ratios of concentrations at which the plateaus occurred, problems associated with variable solution volumes are overcome. The ratios of subsequent plateau levels to the initial value are summarized in Table 3 for the different types of alloys and treatment programmes. Inspection of the data clearly shows that the behaviour of copper, brass and bronze is the same, but that composite materials are somewhat different. The reason why the plateau ratios are the same for copper, brass and bronze lies in the fact that the same mechanism controls the removal of chloride ions. The different ratios found for composite materials are a reflection of the influence of the rate determining steps associated with chloride release from degraded glass and/or iron. On the basis of the data in Table 3 it is now possible to predict how much of the "available" chloride is removed in each stage of desalination. For copper and its binary alloys, the first wash will generally extract approximately 73% of the total, the second wash about 21% and the third wash the remaining 6% (see Table 3).

Although the ratios of plateau levels and the percentage extraction in each wash showed remarkably little variation, the same cannot be said for the treatment times. For copper objects, two months is normally required to remove 72±4% of the chlorides when washing in 1-2 wt% sodium sesquicarbonate. The apparently shorter time required to plateau in deionzed water is partly a reflection of the fact that deionized water will not necessarily extract the same total amount of chloride out of a given object as will other treatments.[1] All washing experiments had a ratio of wash volume to object volume of greater than ten. Bronzes and brasses normally contain larger amounts of chloride ions (see previous section for discussion) and so it is not unexpected that they will take slightly longer to reach the same level of removal than copper objects. With composite materials the first plateau is reached earlier than for the parent alloys since chlorides are removed more rapidly from glass than bronzes.[18] Since several sets of objects required only two washes to stabilize them, there is insufficient data to obtain statistically valid mean values for the times taken to reach the second and third plateaus. Inspection of the data in Table 3 for total treatment times, shows that all types of objects should be stabilized within a period of nine months, with simple copper artefacts typically taking three months and brass-bronze objects taking roughly five months.

Alternative treatments

Because of time constraints many conservators need to be able to speed up the treatment programmes, especially if they are working in private industry. The problem of how to choose the most appropriate technique has recently been discussed[1] but simple comparison of sodium sesquicarbonate and alkaline sodium dithionite shows that, in the absence of aesthetic and materials constraints, the former is roughly ten to fifteen times slower than the dithionite method. Under the action of the alkaline dithionite solution the Cu_2O layer on the surface is reduced to copper metal and this makes the surface structure much more porous. Copper corrosion products within the metal matrix are also reduced to the metallic state and so the major limitation to the rate of chloride removal is the tortuosity (dimensionless path length) of the host material. Under d.c. electrolysis similar chloride release rates to alkaline dithionite are observed. With a direct current, the "reducing power" comes from a source external to the solution.

Conclusion

A mechanism controlling the release of chloride ions from corroded copper/copper alloys has been described and shown to give theoretical values of corrosion depth that are supported by experimental observations. Analysis of the data obtained from treating some thousands of objects has established a series of characteristic chloride release rates that relate to alloy composition and the on-site microenvironment. It is now possible to assess with a high degree of confidence how much of the available chloride ions will be released at each stage of the desalination process. The data base established through analysis of the treatment programmes enables prediction of how long the overall stabilization process will take.

Acknowledgements

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Table 1

Chemical analyses of objects recovered from shipwrecks

	Cu	Sn	Pb	Zn	Fe	Sb	As
Batavia door pintles	92.7	1.4	1.1	0.5	2.1	0.3	0.14
Cumberland pintle pin	63.0	2.37	13.6	20.5	0.82	0.10	n.d.
Lively sheathing tacks	87.08	8.53	0.79	2.97	0.105	0.066	0.01

Table 2

Normalised chloride release rates for stabilization of artefacts during the first wash in deionized water and 1-2 wt% sodium sesquicarbonate solutions in $\mu g.cm^{-2}\ hr^{-1/2}$

Composition	Microenvironment	Mean values of Normalised release rates	No. of data sets
Copper	aerobic	5.9 ± 2.6	12
Brass	aerobic	14.2 ± 5.7	8
Bronze	aerobic	50.1 ± 17.4	7
Composite⁺	aerobic	380 ± 227	4
Copper	anaerobic	1.7 ± 0.6	3
Bronze	anaerobic	12.9 ± 7.0	5

⁺Composite materials included *Batavia* (1629) composite iron-copper-brass-solder cannon,[19] and brass portholes with glass windows from the *Georgette* (1876) and *Xantho* (1872).

Table 3

Mean plateau ratios and treatment times for desalination of copper and its alloys

	Copper aerobic	Brass-Bronze aerobic	Brass-Bronze anaerobic	Composite aerobic
Second wash ratio	0.216±0.031	0.23 ±0.03	0.23 ±0.03	0.370±0.065
Third wash plateau ratio	0.071±0.020	0.065±0.020	0.065±0.020	0.130±0.065
Length of initial wash (days)	64±19[1] 41±15[2]	79±18[1] 79±33[2]	40.3 ±5.6	50.2±16.4
Total treatment (days)	105±71	218±111	166±61	283±12
% Cl extracted				
1st wash	72.0 ±3.8	74.8 ±6.7	-	69.7±7.0
2nd wash	21.8 ±4.7	20.1 ±6.0	-	22.4±4.2
3rd wash	6.3 ±0.8	7.4 ±3.2	-	7.6±2.9

[1]Treatment in sodium sesquicarbonate solutions
[2]Treatment in deionized water

SUMME

auteur présente une pre-
ière série d'essais sur les
vêtements de protection
s objets métalliques. Ces
ssais, effectués dans des
ceintes climatiques
rouillard salin, rayonne-
nt U.V. et chocs thermi-
ues), ont pour but de
terminer quels sont les
vêtements protecteurs les
eux adaptés aux objets
chéologiques métalliques.
s recherches en sont à
ur début et les produits
stés sont encore trop peu
mbreux pour pouvoir tirer
s renseignements défini-
fs, toutefois quelques
sultats sont surprenants.

ETUDE COMPAREE DE LA RESISTANCE A DIVERSES FORMES DE CORROSION DES REVETEMENTS PROTECTEURS UTILISES EN CONSERVATION DES METAUX

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Introduction

Les produits utilisés pour le revêtement des surfaces métalliques, après nettoyage, sont très nombreux. Certains sont bien connus et largement utilisés, d'autres, nouveaux sur le marché ou anciens mais méconnus, ne le sont pas. Il existe, de surcroît, un certain "laisser-aller" des conservateurs/restaurateurs qui ont tendance à ne pas chercher à savoir si un nouveau produit est meilleur qu'un autre ou qui décident, une fois pour toutes, que seul tel ou tel produit est à utiliser dans telle circonstance. De nombreuses publications ont été faites sur le sujet (1) (2) (3) mais très peu se sont préoccupées des réactions des revêtements sur les surfaces métalliques avec, en arrière-pensée, l'application aux métaux archéologiques. C'est la raison pour laquelle nous nous sommes intéressés à ce sujet.
Il n'est pas possible de se procurer tous les produits existant dans le monde surtout à quelques milliers de kilomètres de leur lieu de fabrication. Nous avons donc fait nos essais sur des produits facilement trouvables en Europe et, plus particulièrement en France.
Les essais effectués ne sont qu'un début dans nos recherches et nous sommes parfaitement conscients de leur manque d'universalité. Les prochaines années nous permettront de multiplier les essais et, nous l'espérons, de définir les produits les mieux adaptés aux problèmes des métaux archéologiques.

1. Protocole d'essais

Pour faire nos essais, nous avons pris le parti de n'utiliser, dans un premier temps, que des échantillons neufs, de composition connue. Une seconde équipe, à Nancy, mène des recherches directement sur les objets archéologiques. Nous devrions ainsi définir rapidement si les corrélations entre objets anciens et échantillons récents sont aussi valables que nous l'espérons.
Nos premiers essais ont porté sur des échantillons en fer et en cuivre et pour cela nous avons utilisé trois types de corrosion artificielle: brouillard salin, rayonnement ultra-violet et chocs thermiques. Dans l'avenir, nous travaillerons sur d'autres métaux et d'autres alliages et nous utiliserons également le dioxyde de soufre et le gaz carbonique.

1.1. Préparation des échantillons

Nous avons préparé des éprouvettes de 4 x 4 x 0,1 cm. Elles ont été décapées par sablage avec des billes de verre calibrées de 4 à 45 microns. Le sablage a été effectué à 20 cm des éprouvettes à une pression de 3 kg/cm2 pour le cuivre et de 4 kg/cm2 pour le fer.
Après sablage, nous avons procédé à un nettoyage aux ultrasons dans un bain d'acétone pour éliminer le gras et les billes de verre restantes.

1.1.1. Dépôt des revêtements

1.1.1.1. Première série d'essais

Les échantillons ont été trempés dans les diverses solutions protectrices (tableau n°1) immédiatement après avoir été séchés. Les trempages ont été effectués à froid, sauf pour les cires et la paraffine et n'ont pas dépassé quelques secondes.

1.1.1.2. Deuxième série d'essais

Les dépôts (tableau n°2) ont été effectués sous vide de -1 bar pendant 15 minutes sauf pour les cires et la paraffine pour lesquelles le trempage a été prolongé pendant 5 minutes à 120°C mais à pression normale.

1.1.2. Mesure de l'épaisseur des revêtements

Ce type de mesure est très important car il va permettre de relativiser la protection des diverses solutions. Nous nous sommes, en effet, aperçus que, dans des conditions expérimentales absolument identiques, l'épaisseur du dépôt pouvait varier du simple au double. Les mesures ont été faites avec un Dermitron D8 (Engelhard Industries).

TABLEAU N°1

Produits protecteurs testés dans la première série d'essais:

Fer	Cuivre	Type
Incralac	Incralac	Polymère acrylique
Pentarol 100	Pentarol 100	Polymère acrylique
Rhodopas M	Rhodopas M	Acétate polyvinyle
Sicomet brillant	Sicomet brillant	Vernis cellulosique
Paraloïd B 72	Paraloïd B 72	Polymère acrylique
Blackor	Blackor	Produit anti-rouille
Cire animale jaune	Cire animale jaune	Céride
Paraloïd B 48 N	Paraloïd B 48 N	Polymère acrylique
Synocryll	Synocryll	Polymère acrylique
Paraffine	Paraffine	
Cire minérale blanche	Cire minérale blanche	Céride
Téténal		Produit anti-U.V.
Novérox		Produit anti-rouille

TABLEAU N°2

Produits protecteurs utilisés dans la deuxième série d'essais:

Fer	Cuivre	Type
Sicomet brillant	Sicomet brillant	Vernis cellulosique
Paraloïd B 48 N	Paraloïd B 48 N	Polymère acrylique
Paraloïd B 72	Paraloïd B 72	Polymère acrylique
Rhodopas M	Rhodopas M	Acétate polyvinyle
Synocryll	Synocryll	Polymère acrylique
Cire microcristalline	Cire microcristalline	Céride
Cire minérale blanche	Cire minérale blanche	Céride
Cire animale jaune	Cire animale jaune	Céride
Paraffine	Paraffine	

1.2. Essais au brouillard salin

Ils ont été effectués selon la norme AFNOR X 41-002 (4): dans une enceinte chauffée à 35°C + ou - 2°C, on fait pénétrer une solution de chlorure de sodium à 5% que l'on pulvérise à l'aide d'une buse spéciale à une pression comprise entre 0,8 et 1,2 MPa. La quantité de brouillard produit doit être de 2 ml + ou - 1 ml par heure, elle est mesurée dans des collecteurs d'une surface de 80 cm2. Les éprouvettes sont placées dans la chambre de pulvérisation, la face à tester vers le haut et forment un angle de 20° avec la verticale (pour des raisons pratiques cet angle a été porté à 40° dans notre enceinte).
La durée des essais a été de 144 heures.

1.3. Essais aux rayonnements ultraviolets

Effectués selon la norme AFNOR T 30-049 (4): dans une enceinte refroidie par un système de ventilation pour conserver une température de 60°C + ou - 2°C, les éprouvettes sont disposées de façon à recevoir perpendiculairement le rayonnement sur toute leur surface. La source lumineuse est un ensemble de 3 lampes à vapeur de mercure dont la bande spectrale va de 2500 à 6000 Angströms (5).
La durée d'exposition a été de 144 heures.

1.4. Essais aux chocs thermiques

En l'absence de normes pour les chocs thermiques, nous avons, dans un premier temps, décidé d'appliquer des chocs très sévères. Les résultats ont montré qu'il valait mieux, pour obtenir des résultats plus valables, utiliser des cycles plus doux.

1.4.1. Première série

Cette première série est celle qui a subi les chocs les plus durs. Nous avons pratiqué 88 cycles sur les 100 prévus (à cause d'une panne de l'enceinte) en faisant varier la température de -35°C à +100°C en 30 minutes et de +100°C à -35°C en 30 minutes aussi. Pendant tout le temps des essais, l'enceinte a été maintenue sèche.

1.4.2. Deuxième série

Pour cette série, nous avons testé en faisant varier les températures de la façon suivante: de +20°C à +80°C en 30 mn, de +80°C à +20°C en 60 mn, de +20°C à 0°C en 60 mn, de 0°C à -35°C en 60 mn, de -35°C à -10°C en 30 mn et de -10°C à +20°C en 60 mn. Pendant la durée des essais, l'humidité est restée libre, c'est-à-dire que l'humidité relative a varié constamment.

2. Résultats

2.1. Cuivre

2.1.1. Epaisseur des revêtements

L'étude des épaisseurs des divers revêtements montre une très grande diversité. On constate que le même produit utilisé à des concentrations identiques donne des épaisseurs différentes selon qu'il est déposé par trempage ou par imprégnation sous vide. La paraffine, si elle est appliquée par trempage prolongé à 120°C, ne laisse pratiquement aucune épaisseur sur le métal alors qu'en trempe rapide elle a une épaisseur variable de 4 à 10 microns. D'une façon générale, l'imprégnation sous vide conduit à un dépôt de moindre importance sur les objets, sauf pour le Synocryll et le Sicomet brillant pour lesquels l'épaisseur reste relativement identique.

Epaisseur moyenne, en microns, des revêtements:

Produits	Pression normale	Sous vide
Synocryll	8 à 16	13 à 16
Paraloïd B 48 N	26 à 46	3 à 14
Rhodopas M	10 à 14	1 à 5
Sicomet brillant	12 à 17	12 à 18
Paraloïd B72	10 à 21	4 à 12
Incralac	5 à 8	-
Pentarol	10 à 17	-
		pression normale mais trempage plus long
Cire animale jaune	8 à 20	4 à 6
Cire minérale blanche	3 à 9	1 à 14
Paraffine	4 à 10	non mesurable < 1
Cire microcristalline	-	< 1 à 2
Blackor	2 à 5	-

2.1.2. Résistance au brouillard salin

2.1.2.1. Première série d'essais

Après 144 heures de brouillard salin, seuls les revêtements de Synocryll, d'Incralac et de Rhodopas M ont relativement bien résisté (moins de 10 à 15% de surface corrodée) mais l'Incralac s'est, partiellement, coloré en noir. Les revêtements de Paraloïd B 48N, le Sicomet et le Paraloïd B72 sont devenus totalement noirs, le Pentarol s'est détaché du support, le Blackor et la cire animale jaune sont globalement aussi oxydés que l'échantillon témoin, quant aux revêtements de paraffine et de cire minérale blanche, ils sont plus oxydés que le témoin !

2.1.2.2. Deuxième série d'essais

Après 144 heures, les résultats les moins mauvais (50% des surfaces corrodées) sont obtenus par: la cire microcristalline, le Synocryll et le Paraloïd B72, tous les autres revêtements sont attaqués à 100%.

2.1.3. Résistance aux rayonnements ultraviolets

2.1.3.1. Première série d'essais

Après 144 heures d'exposition aux U.V., on constate, dans l'ensemble, une assez bonne tenue des diverses préparations. Le meilleur résultat étant obtenu par la paraffine qui n'enregistre aucune modification. Le Synocryll, l'Incralac, le Rhodopas M, le Sicomet, le Paraloïd B72, le Blackor et la cire minérale blanche sont légèrement plus mats ou plus foncés. Les autres revêtements sont complètement colorés en noir, le témoin est très oxydé. A priori donc, l'ensemble est assez bon, même après une exposition à une humidité relative de 100%, on n'observe aucune modification.

2.1.3.2. Deuxième série

Après 144 heures d'U.V. et 72 heures en chambre humide: aucune modification pour les revêtements de Rhodopas M, de Paraffine, de cire minérale blanche et de Paraloïd B72. Les autres revêtements sont soit noircis (Sicomet), soit matifiés et attaqués par piqûre (Paraloïd B 48N, Synocryll, cire microcristalline, cire animale jaune).(6)

2.1.4. Résistance aux chocs thermiques

2.1.4.1. Première série

Après 88 cycles: ont bien résisté (pas de changement): le Synocryll, l'Incralac, le Pentarol, le Rhodopas M, le Blackor, la Paraffine. La cire animale jaune est plus attaquée que le témoin, les autres sont noircis et attaqués par piqûre.

2.1.4.2. Deuxième série
Après 99 cycles (plus doux), aucune altération sauf pour la cire animale jaune sous laquelle s'est développée une corrosion par piqûre.

2.2. Fer
2.2.1. Epaisseur des revêtements

Epaisseurs moyennes, en microns, des revêtements

Produit	Pression normale	Sous vide
Synocryll	9 à 16	12 à 14
Paraloïd B 48N	14 à 24	11 à 22
Incralac	3 à 5	-
Pentarol	10 à 29	-
Rhodopas M	11 à 19	2 à 8
Blackor	5 à 13	-
Sicomet	9 à 15	7 à 14
Tètenal	12 à 18	-
Noverox	25 à 40	-
		Pression normale mais imprégnation plus longue
Paraffine	6 à 14	non mesurable
Cire minérable blanche	2 à 7	non mesurable
Cire animale jaune	6 à 13	non mesurable
Cire microcristalline	-	8 à 16

Comme pour le cuivre, on remarque une tendance à la diminution de l'épaisseur des revêtements quand ils sont effectués sous vide. Le petit nombre d'échantillons traités sous vide ne permet cependant pas pour l'instant d'en tirer une règle générale. Le même phénomène se retrouve pour les cires et paraffines qui, appliquées à chaud pendant 5 minutes laissent un dépôt non mesurable.

2.2.2. Essais au brouillard salin
2.2.2.1. Première série
Après 144 heures, les meilleurs résultats sont: le Paraloïd B 48N (moins de 10% de corrosion), le Sicomet (moins de 15%), le Synocryll (environ 35% de la surface corrodée), la cire minérale blanche et la cire animale jaune (40%), l'Incralac (50-55%). Tous les autres échantillons sont corrodés à 100%.

2.2.2.2. Deuxième série
Après 144 heures, nous obtenons deux résultats médiocres (50% de corrosion): le Paraloïd B48N et le Sicomet: toutes les autres éprouvettes sont corrodées à 100%.
Il semble donc que, dans le cas de la corrosion saline, l'imprégnation sous vide ne soit pas souhaitable.

2.2.3. Essais aux rayonnements ultraviolets
2.2.3.1. Première série
Après 144 heures: pas de changement pour le Synocryll, l'Incralac, le Rhodopas M, le Sicomet, la Paraffine et la cire minérable blanche. Le Paraloïd B 48N s'est ridé mais n'a pas changé de coloration, le Pentarol a fortement jauni et tous les autres échantillons sont soit complètement noirs soit attaqués.
Après passage en chambre humide, malheureusement, toutes les éprouvettes, sauf le Paraloïd B48N et le Pentarol,ont été attaquées (corrosion par piqûre démontrant une rupture des monomères).

2.2.3.2. Deuxième série
Après 144 heures d'U.V. et 72 heures de chambre humide: seuls la Paraffine, la cire minérale blanche et la cire microcristalline ne montrent aucune trace d'attaque. Tous les autres échantillons ont été attaqués à des degrés divers (quelques points de rouille pour le Paraloïd B 48N, 100% de la surface attaquée pour le Synocryll).
Le comportement de la paraffine passée à chaud pendant plusieurs minutes est intéressant puisqu'apparemment il n'y a pas d'attaque ultérieure ce qui semble pour le moins étrange étant donné que la couche déposée est moindre que dans le cas d'un passage rapide. Il faudra reprendre l'expérimentation pour pouvoir tirer des conclusions définitives.

2.2.4. Essais aux chocs thermiques
2.2.4.1. Première série
Très bonne tenue après 88 cycles pour le synocryll, le Rhodopas M et le Sicomet; très légère attaque pour le Paraloïd B48N, l'Incralac, la Paraffine, la cire minérale blanche et la cire animale jaune.

Jaunissement mais pas d'attaque pour le Pentarol et le Blackor. Corrosion par piqûre assez marquée pour le Tètenal et le témoin. La coloration noire du Noverox ne permet pas de tirer de conclusion sur ces réactions.

2.2.4.2. Deuxième série
Après 99 cycles, aucun échantillon n'est attaqué. Ce deuxième type de cycle étant plus approprié aux objets de musées, il semble que, dans l'ensemble, les produits testés soient assez efficaces.

Conclusions

Les essais ne faisant que commencer, il paraît difficile de porter des jugements définitifs sur les divers produits testés. On peut toutefois remarquer que:
- pour le cuivre, le Synocryll, l'Incralac et le Rhodopas M semblent les mieux adaptés. La paraffine présente aussi une bonne résistance mais la difficulté de réversibilité réelle nous oblige, pour l'instant à la tenir à l'écart des meilleurs produits. Les variations d'épaisseur enregistrées ne peuvent expliquer que ces trois produits soient les meilleurs.
- pour le fer, un seul produit se retrouve à chaque essai dans les trois plus résistants: le Sicomet. Il est suivi de très près par le Paraloïd B 48N qui est vendu comme adapté précisément aux métaux ferreux, et par le Synocryll.
- l'imprégnation sous vide n'apporte aucun avantage par rapport à l'imprégnation à pression atmosphérique normale, sauf, peut-être dans le cas de la protection du fer contre les U.V. En revanche, la tenue des revêtements est moins bonne en atmosphère saline et ce, quel que soit le métal.

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SUMMARY

he Institute of Material listory of the Polish acade- y of Science organised an rchaeological excavation n Poznań Cathedral. Under he oldest part of the Cathe ral several bishops graves ere found. They date back o XI -XIII centuries. ach grave contained a set f silver chalice, paten nd metallic crossier. he details are given about he technology and scientific xaminations which were carri d out after 1982,usung seve al methods of chemical ana- ysis as atomic absorption, lectron microscopy, micro- robe analysis etc. he conservation of the ro- anesque and gothic chalices nd paten are also described.

THE INVESTIGATION AND CONSERVATION OF EARLY MEDIEVAL SILVER Chalices AND PATEN

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The Institute of Material Cultural History of the Polish Academy of Science organised an archaeological excavation in Poznan Cathedral, during 1952 and 1953.Under the oldest part of the Cathedral several graves were found. Some of them contained pieces of jewellery,a silver paten a chalice and metallic crozier. These attributes indicate that bishops had been buried there.

The silver objects are dated from the second half of the eleventh century to the thirteenth century.The research and conservation of the romanesque chalice and paten were reported during the 7 triennal Meeting of ICOM Commitee.

The purpose of this paper is to document the new conservation process of the following chalices and patens which was carried out 1984 -1986 and to present of a scientific examination of the object.

The aim of the chemical analyses was to find the characteristic chemical composition of alloys used to make the objects and to investigate the technology applied to manufacture the objects. A sepearate question to be solved was the cause of the very extensive embrittlement of the silver.

The methods of analysis used were quantitative emission spectroscopy for major elements and atomic absorption for minor and trace elements. Three different positions were analysed in situ on each object by emmision spectroscopy. For atomic absorption,50mg samples were taken.

The results of chemical analyses are listed in the Table 1.

Table 1
The chemical analyses of gothic silver chalice and paten

object	Concentration %									
	Fe	Pb	Sn	Cu	Zn	Ni	Hg	Au	Ni	Cd
chalice	0.16	0.08	0.2	3.9	0.05	0.02	0.12	0.14	0.02	0.02
paten	0.02	0.5	0.8	9.8	0.04	0.01	0.00	0.01	0.01	0.00

Copper was the major alloying element in all tested objects. The concentration of copper varied from 3.9 % for the gothic chalice up to 9.8 for the romanesque paten.Various amounts of lead,tin and gold were detected.

This chemical composition of ancient silver may indicate the location of the ore and technology used to smelt it.

The usual sources of silver in medieval times were argentiferrous lead ores containing small amounts of tin. Such ores were found in the area of Poland to the north of Krakow. It is probable that the concentration of lead of lead of 3 % in the first romanesque chalice and 0.5 in the paten is derived from the silver refining technology.A small amount of gold was found in the gothic chalice probably as a result of the gilding process. Under a binocular microscope some remains of gold were visibible on the surface. Furthermore the presence of 0.12% of mercury in the silver proves that the fire-gilding process was applied for gilding of the gothic chalice.

More technical information about the investigated objects was obtained from a metallographic examination.

Sampling is always the most difficult problem in testing of ancient objects. This is because the ancient alloys are often somewhat inhomogenous on a microscopic scale. Therefore, the availability of only a small number of very small samples is a limiting factor in obtaining proper conclusions concerning technical details during the investigation of rare ancient objects.

Fig.1.Gothic chalice. Ortho rombic sulphides. SEM.4700x

Fig.2. The paten. Characteristic dendrite of α . SEM.4700x

Fig.3. The gothic chalice. The stem consists of two barrel-like parts and rings

The inhomogeneity of siver-copper alloys depends on the manufactu ring which controls the size and distribution of the phases.The higher the purity of the silver,the less is the inhomogeneity problem.In fact, we can consider that up to 5% Cu concentration in silver is to maximum to avoide technological problems during the production of silver objects. In addition, the presence of copper will contribute to a natural ageing processs of the silver due to the precipitation of copper rich phases which decrease the plasticity of ancient silver objects.

Samples of metal for metallography were taken from the broken edge of the bowl and the base of the chalice and paten.
The polished cross sections and fracture surfaces were examined under the optical microscope and in the scanning electron microscope.During the SEM examination X-ray microanalysis was used for detection of the elements concentrated in observed areas.The copper concentration in the gothic chalice was up to 10% / locally/ and produced the microstructure consisting eutectic and α phase. Brittleness of this object is mainly due to intercrystalline corrosion.

The presence of many non -mrtallic inclusions,identified as comlex silver -copper sulphides,accelerated the corrosion process by setting up corrosion cells with silver.Great number of dimples probably produced by sulphides are visible in a fracture section which is on the Fig.1.

The eutectic structure of the Ag-Cu system consists of silver-rich and copper -rich phases. The electrochemical potential between these two phases is the natural cause of the corrosion process.As the rsult of the casting of copper -rich silver alloys,the eutectic exhibits a special type of cell structure which also plays a role in the selective dissolution of metal.

The corrosion processes were accelerated because of amine compound originating during the decomposition of human bodies in close contact with the metallic objects.

The microstructure of the paten shows some porosity due to casting The corrosion pitting is quite deep. Dendrites are visible on the surface on the surface of the paten even at a low magnification as can be seen in the next Fig.4

The dendrites have a characteristic distribution of silver and copper. The silver content increases towards the centre of the dendrite,so the centre is more cathodic than the peripheric areas. Hence,the edges of the dendrities undergo corrosion faster than other areas.

The brittleness of the paten was caused by advanced corrosion process and the presence of detrimental multieutectics distributed at the grain boundaries, probably combined with natural ageing proces This natural ageing process is well known for silver-copper alloys where very fine intermetallic particles are precipitated from soli solution along the grain boundaries.

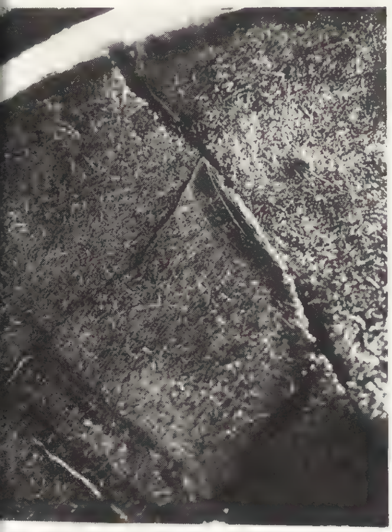
The paten was made by means of casting followed by slight hammering and finished by engraving.This is clearly visible on the hand and vertical arm of the cross.The outer circles was polished after the paten was embossed.

The gothic chalice was made by a spinning technique.The stem consists of two barrel-like parts and rings 5 mm wide soldered togeth which can be seen in the Fig. .Geometrical patterns decorate the surface around the base.The design was either embossed in a repoussémanner or by hammering onto a mould. The outline of the decorative motives indicates that wooden punches or wooden stamps may have been used.

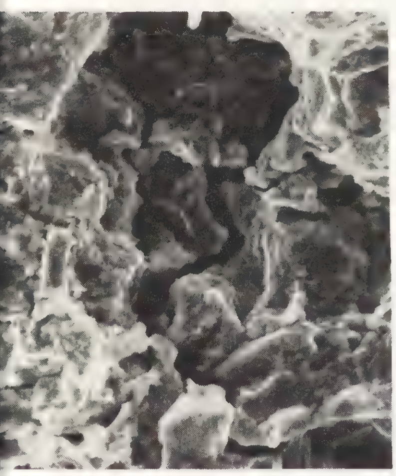
Guite large areas of the stem of the bowl and of the base appear to have lost their covering of gold and a thin layer of gold is now only visible an small areas of the object.

The silver objects found in Poznan Cathedral were probably produced in different periods and it is difficult to establish where they were made.The chemical composition,especially as regards the lead,probably indicates that these silver objects were produced locally in Poland.

The technique of forming the objects was very well known and could be performed by local silversmiths. However,from the 12th century, very skilfully made and ornamented chalices were imported into Poland from Western Europe.Our chalice,are modest in appearance and were made by simple techniques. They were known as"calix viaticus" and were used when travelling or for putting into tombs.



ig.4.The paten. Dendrite isible on the surface.5x



ig.5.The paten.Fracture surface with visible cracks covered by corrosion product SEM .4700x

An early conservation treatment performed in 1960 by the State La boratory for Conservation of Antiquities in Warsaw consisted of the removal of corrosion deposits, the re-shaping of distored frag ments and the filling of gaps.Each part of the object was reshaped at room temperature and joined together with butylmethacrylate ad-hesive. Missing part were reconstructed using 1mm thick celophane tape glued to the orginal metallic part,then the whole surface was covered with butyl methacrylate in the inside or on the back.

About 15 years after the first conservation process the crylic sup port started to become more and more distorted.

The first stage in the new conservation treatment of these objects consisted of the removal of the acrylic resin by means of swabs in acetone. A mould and areas of deformation were corrected during the moulding process by use of pieces of modeling clay-sulpur free. The mould were removed from the objects and used as formers for rebuilding the objects from the fragments as they were released from the previous restoration by the acetone swabs.

The rebuilding was especially difficult for the gothic chalice whe re the edges of the fragments of silver were extremaly thin,corrod ed and brittle.It was impossible to join them together directly and so polyester resin and very fine glass fibre matting was used to bridge across between the fragments.

The second stage of the restoration was devoted to filling the missing areas. For this purpose pieces of glass fibre matting were also used,and the fibre matting was made a little larger than the gaps so that it overlapped the edges of the lacunae. The glass fibre was impregnated with polyester resin and positioned on the gap of the supporting model made of silicone rubber. After this had hardened,futher small portions of polyester were added by means of a brush until the thickness of the restored gap reached the thichness of the surrounding metal.

When the process of filling gaps was completed the silicone rubber mould was removed.The restored areas were then filled up to exact countour of the outside of each object by adding more resin as ne-cessary. Because of the very many small pieces into which the bowl of the gothic chalice has desintegrated it was finally necessary to line it completely on the inside with glass fibre and resin. The finishing touches involved minor correction of the stage and some decorative motives.

The final stage of the treatment was colouring of the restored areas,with silver flake applied with commercial adhesive which is usually used for the attachment of gold leaf to other object.

RESTORATION OF A LEAD-LINED GLASS WINDOW FRAGMENT RECOVERED FROM A 14TH C. EXCAVATION

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SUMMARY

The 14th century lead-lined glass window fragment, excavated in Esztergom was in a very bad state of preservation. The object was crushed into a single entangled bundle.

The cleaning in heated acid solution lead not only to the softening of hard corrosion layers but also made possible the careful unfolding of the leadinq. Lead was used for the completion and reconstruction of some missing parts of the leading and polyester resin for the glass.

1. Introduction

On the origins of the object
The find was discovered in a drainage ditch near the stairs of the Basilica on Castle Hill in Esztergom. The Basilica which is the greatest church of present-day Hungary, was erected in the 19th century on top of the ruins of St. Adalbert's Church established by the first Hungarian king, Saint Stephen at the beginnin g of the 11th c. During construction the ruins of the ancient church were used for groundwork and, as a result, a lot of valuable architectural relics were buried underground. The unearthed lead-lined window fragment is one of our few mediaveal relics. It probably dates back to the 14th c. when according to written sources Bishop Thomas borrowed huge sums of money for the renovation of the ruined church, although construction contiuned of the original church well until 1321. Merit for the full reconstruction and rebuilding /1330-1349/ is due to Csanád Telegdi's.

As the Chronica Hungarorum Acephala reports:
"....He had the chapel of the cathedral named after the martyr Saint Adalbert completely rebuilt by carved and broad stones, beautifully decorated columns, firm pedestals and wonderfully faced beams, a magnificent vault according to the best techniques known in architecture, and completed it by glass windows and fortifications outside".

Other literary sources claim that Csanád Telegdi had craftsmen borught in from Kassa who then made some richly decorated stained windows and plain ones to let the light in, for churches around.

/Fragments of a stained glass window were also recovered in the Castle hill, but at another site and at another time. The colour of the glass is yellow ochre and cobalt blue./

2. Restoration of the window

2.1. The condition of the object before restoration
The leading was found to be in a very poor condition when brought to the restoration workshop. At first sight neither its size nor the shape of the motifs could be determined as the object was crushed into a single entangled bundle with an iron bar of about 50 cm corroded into it. The surface of the lead was covered by a greyish-yellow corrosion layer, the metal itself, however, was fairly firm. /See Figure 1/

Fig. 1: The object after excavation

There were some small-sized, uncoloured glass pieces braced by the leading.

2.2. The process of restoration:
The object was made of several materials, and when describing its restoration each component will be considered separately.

Lead:
Cleaning: Dirt from the soil was removed with a 10 % solution of potassium-hexametaphosphate. Since the melting point of lead is very low /327 °C/ and it expands at a low temperature, which makes the unfolding of the object easier, the first cleaning procedure was treatment with a 10 % solution of acetic acid heated to about 80 °C. After soaking it for a short while /30 minutes/ the object was neutralized in ammonium hydroxide and dehydrated in a 96 % solution of alcohol. The process brought about better results than expected, since the object was cleaned of much of the hard carbonate layer /which had considerably increased the brittleness of lead/ and made the careful unfolding of the leading possible.

Technical observations:
After unfolding it was already perceivable that the size of the window fragment was about 80x50 cm. The pattern of motifs also became clearly discernible /See Figure 2/. The lead rings wer separated by one unit from each other and after soldering a circular-triangular pattern evolved. There were straight lead lines showing the dimensions of the window on the longitudinal edges of the fragments. In the small triangles a couple of intact glass pieces were found scattered about; these had to be removed for the purposes of cleaning. When examining them it was easy to recognize that they had been cut to the appropriate size by the application of an ancient technique: a pointed and heated iron bar was pressed strongly onto the surface of the cooled /wet/ glass which cracked owing to the great difference in temperature. Their surface is not the same and the size varies as well. These glass pieces were most probably manufactured in glassworks by casting since their thickness differs from each other. /See Figure 3/

Restoration - Completion:
In order to flatten the rings, semicircular templates of the required size /10-11.5 cm/ were prepared from fibre slabs whose thickness /5 mm/ was chosen to correspond to the inner width of the leading. The field was not uniform, it was broken in a number of places and relatively extensive pieces were missing from the middle. Considering the fact that an archaeological rarity was involved, I consulted the archaeologist directing the excavation and decided that my task should go beyond conservation and that I should aim at trying to make the object suitable for exhibition. The missing fragments were replaced by the same material /lead/ and prepared in accordance with the original size /5 mm wide and 5 mm inner width/. In the course of restoring the metal no alien materials were applied for adhesion or completions. The frame was assembled following the way it had originally been made, yet the original and the completed parts are easily discernible. /See Figure 4/.

Choosing the right method for completion was facilitated by consulting and instructions of the specialized literature, as well as the employment of the original tools of the craft. /See Figure 5/.

Fig. 3: Original pieces of the glass

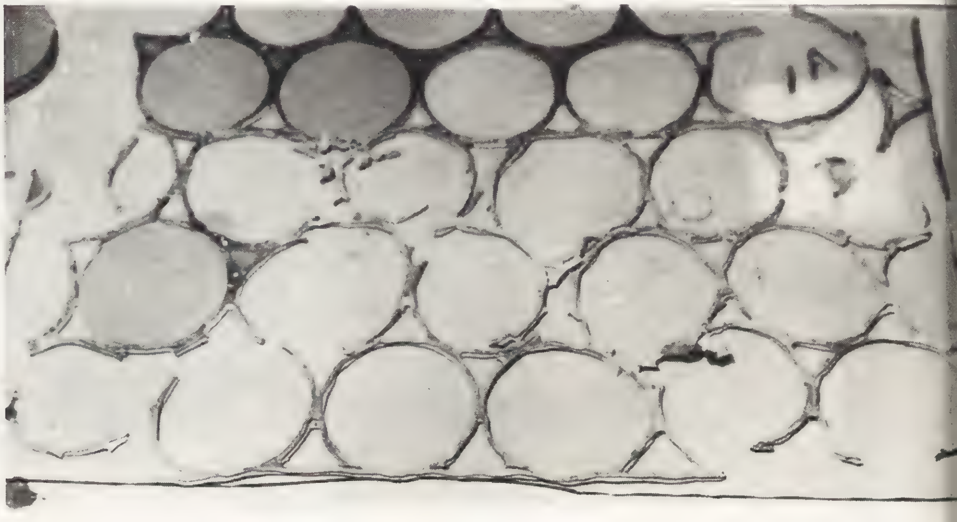

Fig. 2: The outstreched lead frame

Fig. 5: Tools of the window-making artisans

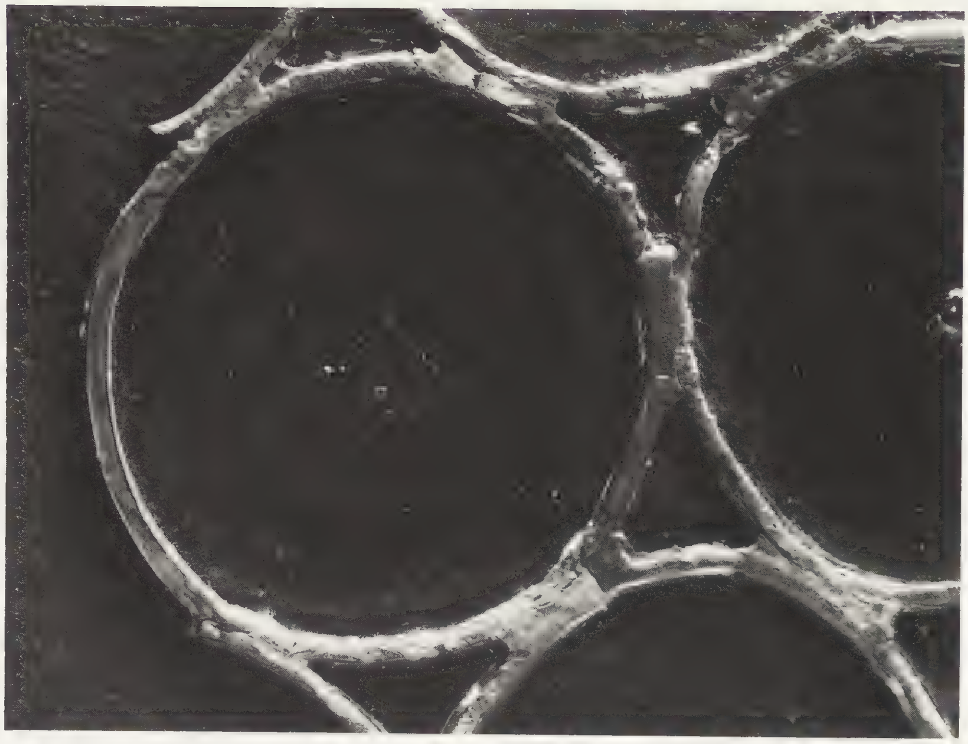

Fig. 4: A part of the completed lead frame

Lead to be used for completions was bent to the required curve with the help of the template following which it was built in by soldering. This proved to be a lengthy and involved task since one had to take care that the original solder should not melt and only the minimum amount of solder be applied, still bringing about a firm locking together of the rings. /The work was carried out on both sides of the window /.

Glass

Cleaning: Cleaning of the original glass pieces was done with a 10 % solution of hydrofluoric acid. The firm glass was found to tolerate the treatment well. After having rinsed it repeatedly with distilled water the glass was dried and conserved by polybutylmethacrylate. The result is a transparent, uniform glass surface.

Restoration - Completion:

The already cleaned and conserved glass pieces were put back in their original places continuously. The next phase of reconstruction was to re-create the complete outlines of the window. After experimenting with various methods replacement of the missing glass was carried out as described below.

The leading was placed on a levelled wooden panel covered by aluminium foil. The circles and triangles were filled up by a two component silicone-caoutchouc /Wacker Siliconkautschuk Giessmasse 56+Härter T/ substance as high as the bottom rims of the leading /See Figure 6/. This was necessary to prevent the synthetic resin flowing from one field to another through the minute cracks and somewhat uneven lead. After the setting /polymerization / of the silicone, replacement of the missing glass pieces could commence. For this purpose a twocomponent polyester resin /VIAPAL F-120/ was employed. The resin had to be cast in several layers since the shrinking of polyester resin after polymerization is considerable. /See Figure 7/. Slow polymerization made it possible to finish the completed surface and give it an archaic look to imitate old cast glass. After the elapse of 24 hours the window was turned over with the foil and the silicone layers used as auxilliaries removed. The conservation of the iron bar attached to the window and with no metal core remaining, followed.

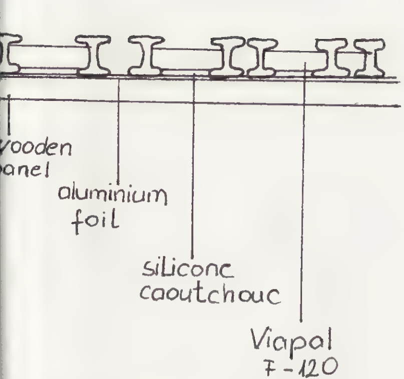

Fig. 6: The filling up of the circles and triangles

Iron:

Cleaning: Dirt from the soil was removed with sodium hexametaphosphate following which the weak iron, whose cleaning to the metal core was impossible, was dechlorinated using a 10 % solutin of NaOH.

Conservation: After passivation by phosphoric acid, conservation was carried out with Paraloid B 72 containing graphite powder.

The bracing iron which was employed for firm support was fastened to the window by lead clamps. The iron bar was placed back into these clamps and the restored object was fixed to an appropriate mounting./See Figure 8 and 9/.

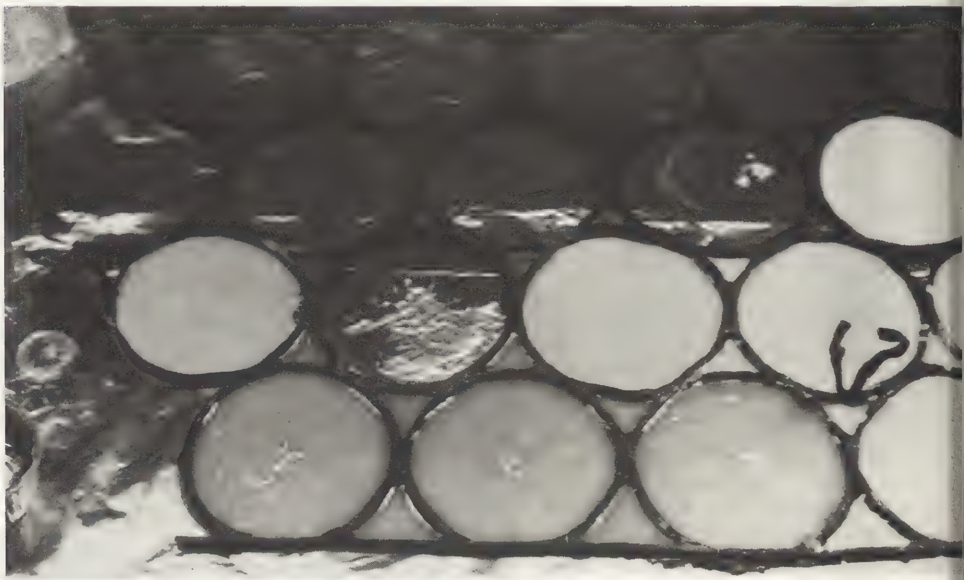

Fig. 7: A detail of the completed glass

Fig. 8: The lead clamps which fastened the iron bar

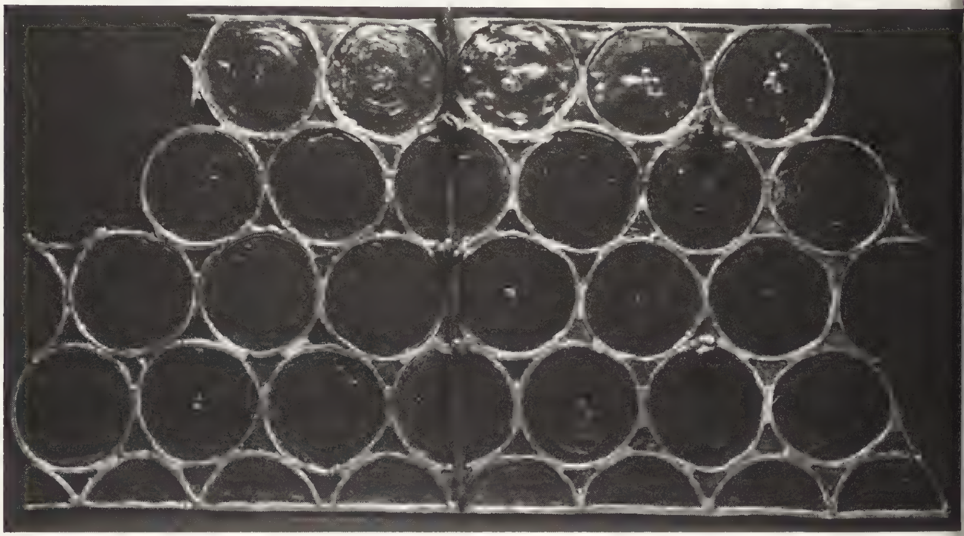

Fig. 9: The reconstructed object

3. Conclusion

By the help of the procedures described the aesthetic value of the object was restored, and hopefully, the life of it lengthened. This fact can be evaluated the better with a view of the extreme scarcity of such finds in Hungary.

Acknowledgements:

My thanks go to István Horváth, archaeologist and Zoltán Szalay, restorer and to Tibor Bráda, professor in the Art College for their valuable professional advice.

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Working Group 23

Icons

Icônes

THE TECHNICAL EXAMINATION OF RUSSIAN ICONS AND OKLADS

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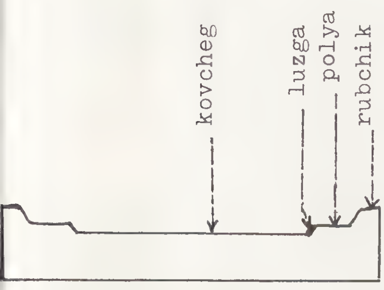
SUMMARY

This paper outlines a general method and use for technical examinations of Russian painted panel icons and metal oklads and some related conservation problems. A brief review is also given of examinations of selected Russian icons in the United States. The author calls for thorough documentation before authentication and a discussion of ethical and technical concerns for conservators of these Russian religious objects.



An Icon Support

INTRODUCTION

From foreign invaders, to civil and religious upheavals, to cries of "fake" or "masterpiece" the Russian icon has survived centuries of human turmoil and foible as a silent witness of a peoples' faith. Russian icons are unique religious art forms which traditionally were created by the faithful and for the faithful to be used in the church or home according to the tenets of their Christian belief.

In a broad sense, old Russian icons had similar physical characteristics up to the beginning of the 17th century, following traditional structural forms, material components, artistic styles and doctrinal subjects with variations according to the century and geographic locale where they were made. After the mid 17th century, Russian icons sometimes reflected physical and artistic aspects of Western culture as well as the ecclesiastic, social and economic changes of their day.

Russian icons were first brought to North America by 18th century Russian traders and missionaries to Alaska. By the late 19th and 20th centuries, they were displayed in Russian, American and European museums, trade fairs, private collections and commercial art galleries, not only as a testimony of their universal artistic appeal but now also as objects of secular commerce.

THE TECHNICAL EXAMINATION

The technical examination is important for those concerned with the preservation and documentation of Russian icons such as conservators, art historians and museum curators.

Except for conservation purposes, technical examinations are seldom requested for an icon in active religious use. Russian Orthodox, Old Believer, Byzantine Catholic and other Eastern Orthodox faithful in the United States often use old Russian as well as modern hand-painted icons, composite icons of various materials and even reproductions made of paper and synthetic polymers, as long as they are canonical and blessed.

The primary reason for a thorough technical examination of icons and their metal covers (oklads) arises from the need to study the material and structural components and the extent and nature of their physical deterioration in order to formulate compatible conservation treatments. Using a stereo-binocular microscope with fan-cooled fiber optic illumination, a 35 mm. camera with a macro lens, X-radiographs, micro-chemical tests, an ultra violet light and detailed macroscopic observations, this type of methodical study also functions to confirm historic, ethnographic, physical and structural information.

The overall examination of an icon and oklad may vary according to the object but should include such basic facts as:

Date of examination; subject of the icon; translation of Old Church Slavonic writing; identification or accession numbers; measurements (3 dimensions); name of the owner; provenance; history (date and place of acquisition, place of exhibition, restoration or conservation treatments, previous photographs, etc.) and a complete written description as well as overall and close-up color photographs or slides of the bare verso and the painted recto both with and without an oklad. The front and reverse of the oklad should also be examined and photographed to yield the above information.

Examination Of The Icon Begins On The Bare Verso with attention to the number of boards and how they are joined; woodworking marks; color of wood--stained or natural?; preliminary identification of wood; placement and number of any nails, screws, holes, etc.; notations of labels and Cyrillic writing (translated); ethnographic deposits; placement, dimensions, type, color and number of slats (shponki); examination of the edges for nails and their placement and a complete condition report.

Examination Of The Painted Recto includes a description of the construction of the support including measurements of all carved surfaces such as the outermost margin (rubchik), the raised border (polya), the inclined dip (luzga) and the central area that receives the main painting (kovcheg); a complete description of all other layers such as the cellulosic (linen or paper) layer; the ground layer; the metal leaf layer (gold, silver covered with shellac, etc.); the paint layer (colors, preliminary identification of pigments and binding medium); Old Church Slavonic writing with translations; the varnish layer; ethnographic deposits or evidence of ethnographic use; evidence of previous restoration or conservation; details of the microscopic examination; a complete condition report of the painted recto; data from the X-ray radiograph such as number and location of nail holes or hidden nails, reconstruction or additions to the support, distribution pattern of radio-opaque pigments, type of weave and placement of linen layer, fragmentary or whole underpainting and any pertinent material analyses or testing.

Examination Of A Metal Oklad investigates the front and the reverse to determine method of manufacture such as remains of pitch, sand or ochre from the repoussé process and other production clues; evidence of gilding or silverplating; evidence of copper or other metal corrosion products; testing of the metal; notation of hallmarks or dates; examination of additions such as a crown (vinetz) or pendant (tsata) to determine if original to the oklad; nails, nail holes and their placement; and evidence of ethnographic use such as from kissing and touching (as suspected by the formation of corrosion products and/or the pattern of wear of the metal in specific areas) or lighting candles (wax drippings; formation of copper oleates). A thorough condition report should reveal structural damage or physical alteration as well as existing or potential problems due to the exhibit environment or human handling.

After the material information has been documented by writing and photography, it is analyzed to determine objective facts about the icon and oklad. This knowledge allows the conservator to formulate conservation treatments and recommendations for exhibit or travel. When this physical data is correlated with the religious context and artistic style, then a comprehensive study of the icon and oklad begins to emerge, giving the art historian and museum curator a basis for responsible authentication.

PROBLEMS IN ICON CONSERVATION

Some conservators and restorers, unfamiliar with icon materials and properties, have used excessively harsh treatments. In the past, pumice was sometimes used to remove an oxidized linseed oil varnish layer with resultant abrasion of the paint and delicate gold leaf layers. Chemically inappropriate solvents used on a darkened varnish layer may reveal that some 18th and 19th century icon painters intentionally covered silver leaf with shellac to produce a golden color in imitation of a gold leaf. Often, after this type of treatment, only traces of a silver layer remain.

In the course of an icon examination one may find that waxes, both of a natural low molecular weight and a high molecular weight synthetic composition, have been used in conservation treatments. Waxes generally are inappropriate consolidants for icons as they normally differ from the elements on an icon, change the refractive index of the paints, attract and hold dust and darken the colors by preventing the diffusion of light. They are irreversible after complete impregnation and change the character of an icon so it no longer resembles the original in color, texture and weight. A thin surface application of wax is also not physically stable as microscopic examination of aged wax films will show that some synthetic microcrystalline waxes are brittle, crack and slough off the surface, creating a new type of laminal disruption.

Another problem encountered is lack of knowledge of traditional icon construction and its physical function. One example is a case where the bare verso of an icon had radio-opaque deposits which showed up on a roentgenogram and were interpreted as an underpainting. Without testing the deposits and questioning their relationship to the icon, the conservator removed them by planing the surface and then varnishing the wood. The wooden shponki were removed and discarded because they were perceived as constricting the panel. This treatment served to remove evidence of deliberate alteration and to deprive the support (which was genuine) of its functional slats.

A well-seasoned limewood (Tilia europea) traditionally was the favored wood for old Russian icon supports because of its resistance to insect attack, warping and splitting. One of the most surprising features of genuine, well-made old Russian icons made of limewood is the stable and relatively new appearance of the wood. Forgers sometimes use worm-eaten or distorted wood as icon supports so that the finished product looks more "antique".

USING THE TECHNICAL EXAMINATION

Unfortunately, not all icons which are said to be "Russian" were made to be used as objects of veneration and many of these spurious commercial products proliferate in the United States today. Their source is varied, coming from counterfeiters in the United States and abroad. Because their inferior material components and construction deteriorate rapidly, these are often brought to conservators for treatment. This type of icon frequently does not follow normal patterns of deterioration consistent with the stated age. Sometimes deterioration is artificially or artfully accelerated, as when laminal disruptions are painted on the surface to make an icon appear old.

Some counterfeit icons are made of 2 or more parts which have been combined to make a whole. One may see a "put-together" icon where the painting is old and the oklad new. The new oklad may have hallmarks pretending it is silver or gilded silver, but testing the metal or visualizing copper corrosion products (sometimes seen only microscopically), often demonstrates that the hallmarks were added to deceive the buyer. Sometimes an oklad is constructed of old and new pieces or an old oklad is put over a new painting. New icons have been painted on old supports where almost all of the original painting had deteriorated beyond conservation. A majority of these icons were never made "by the faithful and for the faithful" with the holy in mind, but solely for commercial gain as were some scores of "Russian" icons in a case of fire in which an old woman died. When the insurance company had the icons examined to determine the amount of damage sustained, it was discovered that some of the icons were "put-together" such as previously described. The insurance paid off part of the claim rather than become entangled in a legal battle and the owners kept the largely unharmed icons which were then free to be put on the market again.

In a case of "ire" the monetary value of a divorcing couple's icons was in dispute. The prosecution tried to prove that the defendant willfully damaged them and that her share of the family home should be forfeited to pay for restoration charges. Careful examination of the icons showed that there was no willful damage, but only a normal pattern of deterioration due to environmental factors. In addition, the examination showed an expensive "19th century" icon to be a paper picture (from a fairly recent calender) pasted on wood while another "20th century Greek provincial icon" had actually been painted by the defendant's Russian mother a few years before.

Several years ago the majority of the George R. Hann Russian icon collection, purchased in the Soviet Union and brought to the United States in the 1930's, was called "fake" after it was sold at a record-breaking auction in New York. The icons were purchased by collectors from North America and Europe and some of the new owners became concerned about the validity of this pronouncement made solely on the basis of a pre-auction viewing.

The Timken Gallery of San Diego, California had their 3 newly-purchased Hann icons subjected to technical examinations with detailed X-ray radiographic studies and material analyses performed by several specialists who worked both singly and as a co-operative team. The Ascension was found to have an outer restored support of later origin than the central painting, but the majority of the icon was constructed and painted with materials traditionally used in Russia during the 16th and 17th centuries. This icon has a 12,060 GTG (Government Tretyakov Gallery) label on the reverse and may be part of the I.S. Ostroukhov collection of the same accession numbers, a fact which could be traced through the records of the Tretyakov Gallery. The biographical icon of St. Basil was found to be compatible in materials, techniques and structure with Russian icons of the late 15th or early 16th centuries. The painting had apparently undergone some harsh cleanings and cyclical restorations as was evident in the microscopic examinations. The Nativity was found to have a simulated pattern of deterioration and was an icon painted to appear old. In all three cases, technical examinations were able to factually refute specific, unfounded claims.

CONCLUSION

Technical examinations systematically study the physical aspects of icons and oklads, assisting the efforts of conservators, art historians and museum curators, and should be the foundation for any serious authentication process. The ultimate benefit is derived from the conscientious documentation and preservation of these unique objects which represent the religious beliefs, culture and history of a considerable segment of the world's population.

The problems presented are only a few made evident through the use of technical examinations in the United States as applied to Russian icons. Perhaps the Icon Group of I.C.O.M. can address these technical and ethical concerns and develop guidelines for the icon conservator in today's world.

A SHORT GLOSSARY OF RUSSIAN ICON TERMS

Basma: A thin gold or gilded silver stamped ornamental sheet. When used to form early Russian oklads, these strips were nailed to the recto and edges of an icon.

Dvoinik: A thin leaf of gold beaten onto a silver leaf base. Used on icons beginning in the sixteenth century.

Filyenka: A narrow painted stripe around the periphery of an icon.

Kovcheg: The central excised, or otherwise defined, area of a panel which receives the main painting of an icon.

Luzga: An inclined edge (dip) between the kovcheg and the polya of an icon.

Oklad: A decorative cover for an icon, generally with open areas for exposure of the face, hands and feet of the figures. Often made of silver, gold or copper alloys by repoussé and chasing, but also made of other materials such as textile with embroidery, pearls and gems, etc.

Polya: A flat or raised border surrounding the kovcheg of an icon.

Riza: Thin, decorative metal sheets nailed to, or otherwise placed on certain sections of a painted recto to embellish or emphasize selected features or figures of an icon.

Rubchik: A narrow, carved and raised outermost margin of an icon panel.

Shponka: A wooden slat on the bare verso of an icon inset into the panel to keep the component boards physically united and to retard warping. Shponki is the plural form.

Tsata: A crescent-shaped decorative yoke suspended below the chin. Sometimes used as an ornament separately attached to figures on an oklad.

Vinetz: A halo-like crown sometimes separately attached above the heads of figures on an oklad.

SUMMARY

A description of the intricate restoration of the important Ryazan icon is offered herein. For the purposes of neat discriminations the layer-by-layer contact X-raying has been carried ont due to which the underlying layers and the degree of their preservation are now estimated. After very fine cleanings it became possible to reveal original features of ancient artistry together with aesthetic and iconographic particulars. The original background had been covered with silver, to day preserved only in microfragments. The completion of the restoration process enabled the restorers to claim the hoarest antiquity for the said icon, esteemed to appear as the most ancient not only in Ryazan but also in the Old Russian art as a whole.

THE RESTORATION OF "HODEGETRIA" MOTHER OF GOD ICON FROM RYAZAN - AN INTRICATE CASE OF THE DESCRIPTION OF A MONUMENT WITH A CONTROVERSIAL DATING

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The works of visual art that have survived to our days since the initial period in the history of the Principality of Ryazan are few and far between. Many monuments of the material culture, icons including, perished in the numerous wars and the fires that accompanied them.

It has been considered until recently that all early works of easel painting from Ryazan, mentioned in legends, chronicles, and other written sources are lost irratrievably. However, the restoration of the icon "Hodegetria" Mother of God from the Ryazan Historical-Architectural Museum and Reservation that has been carried on in recent years suggests that this icon, most famous in Ryazan, has survived the Mongol invasion, the internecine wars, and come down to our days.

The "Hodegetria" Mother of God icon was selected for restoration by the All-Russian Artistic Scientific Restoration Centre named after Academician I.E.Grabar from the stock of the Museum in 1975. In the Museum the icon was dated by the 16th century. Experimental clearings were made on the icon at various times already in the Museum. One of them, left of the head of the Mother of God reveals ochre colour of the nymbus and light-green - of the background; two other rectangle-shaped clearings made on the icon borders have revealed the ochre under olifa (drying oil). On the basis of the fragments thus revealed by the experimental clearings, the icon can, indeed, be dated by the 16th century. But the X-raying of the icon that was made before the restoration began indicated that it could be dated still earlier and that the earlier experimental clearings whose places were selected at random coincided with the fillings-in of the later renovation ground. As a result of such random selection, the error in dating was thus confirmed.

The X-raying that was carried out by L.I.Bashmakova indicates that repairs were made, in the first place, in the icon's wooden support. The two inset slats and the two "dovetail"-type slats which can be found today on the reverse side of the icon and which are covered with a thick coat of gesso ground are of later origin. It can be considered that the panels were fastened together by means of those slats in the 17th century, when the gesso ground was laid on the reverse side of the icon, and the composition "Adoration of the Cross" was painted upon it. As it was shown by the X-raying, the reverse side of the icon did not carry the gesso ground coat, originally. The two panels had been fastened at the upper and lower ends of the icon by the still existing overlaid slats held in place by wooden pegs; overlaid horizontal slats were also in the reverse side of the icon. The latter do not exist today, and they were, according to L.I.Bashmakova, 5 cm in width.

With the aid of the layer-by-layer contact X-raying it has been possible to identify the underlying layers and the degree of their preservation. It has come to light that the linen-weave fabric was laid all over the surface of the icon. And this layer is cut out together with the ancient gesso ground on the edges of the margins, on the inset wooden slats on the upper and lower edges and along the joint between the two panels. The presentation of the faces of the Mother of God and the Infant is different from that on the upper coat of paint. The filling-in of the new gesso ground runs all along the joint between the panels, i.e. right across the central line of the face of the Mother of God. The X-raying has shown that the fingers of the right hand of the Infant, the left arm of the Mother of God and the Infant's legs were lost. Besides, all over the surface of the front side of the icon, there have been found small repairs, and also nails and nail holes in a great number. The losses of the fabric, gesso ground and the fillings-in of the later ground, as also the presence of numerous nails of various types-all go to show that during the time the icon has been in existence it was renovated many times. The particular features of the

icon support, the pattern and the nature of fillings-in on the faces of the Mother of God and the Infant, all of which has been detected in the course of the X-raying, suggest that this icon was originally painted not later than the 14th century.

The layer-by-layer removal of coats on the front side of the icon began after the necessary conservation work was accomplished.

The number of layers in the background was determined with the aid of the experimental clearing down to the original layer. This clearing was made in the background and touched the shoulder of the Mother of God. The uppermost layer of the paint in the background, and the borders of the icon was made with the ochre mixed in olifa. As a measure of protection of the uppermost coat of paint from destruction, pieces of mica were inserted into it and, namely, on the face and the right arm of the Mother of God and also on the face and right and left arms of the Infant. This uppermost layer which was the fourth one, beginning from the original, was easily removed with a cotton wad wetted in a respective solution. The mica was carefully removed with a scalpel. The uppermost coat and, respectively, the time of the latest renovation of the icon can be dated by the end of the 19th century.

After the uppermost layer was removed completely, it was found that the Mother of God with the Infant were presented in the third layer against the background of ivory bone colour which was in a good state of preservation. In the third layer the borders were covered with a light ochre and were accentuated with the brown boundary line. The veil of the Mother of God are painted in mat dark green, while the highlights on it - in red brown. The stars on the veil of the Mother of God, the ornament on the border of the veil and on the sleeves, the assist on the Infant's tunic, the contour outlines on the nymbus and the cross on the nymbus of the Infant are painted in a solution of gold. In the painting of the nymbuses, there is a gradual transition from dark ochre along the outer contour to dark rose colour around the heads of the Mother of God and the Infant.

The inscriptions bearing monograms of the Mother of God and Christ are large and painted in dark red-brown colour.

The manner of painting, the colour composition, the special thoroughness with which the assist on the Infant's tunic is painted, the calligraphic accuracy with which the nymbuses are outlined, and especially, the system of letter writing it the monograms, make it possible to date the third coat and, consequently, the penultimate renovation of the icon which was done with a great professionalism by the 70's of the last century.

The next, third coat of paint, was removed mechanically because it was found impossible to select a respective solvent which could soften it. All along the perimeter of the margins, there came to light under the third paint considerable fillings-in of the renovation ground which was laid at the same level with the second layer of paint. The lower margin was a mosaic of various fillings-in of paint which were placed at various times and consisted of several layers of paint.

In the background, the colour of the second layer consisted of the light ochre mixed with the whiting and the borders of the icon were painted in red ochra. There came to light the nymbus painted in light golden ochre and outlined in red-brown, and the stripes of the cross on the nimbuses were painted in red-brown. The locational pattern of the letters "MP" "ΘY" and "IИC" "XC" differed from that on the higher layer. The letters are painted in cinnabar, and they are considerably smaller in size than in the third coat. "MP" and "ΘY" are raised rather high and almost reach the dip. The location of the letters "IИC" "XC" coincides with those in the third coat of paint but they are painted in a more compact manner. The images of the Mother of God and the Infant were not repainted during the second renovation.

It should be noted that it was precisely this coat that was "opened" in the course of the experimental clearings in the Museum. The colour of the background that was revealed in the course of those clearings looked greenish because the layer of the darkened olifa nad not been removed completely. On the basis of the small fragments of the painting which was thus revealed, one could date the icon approximately by the 16th century but when the layer was opened completely it became possible to more exactly date the second renovation by the 17th century. The la-

ter dating is confirmed by the nature of the letter designation of the Mother of God and Christ, by the colour of the outlines of the nimbus sand the crosses on them and also by the colour of the margins. The author of the present study has never come across cases when Christ's monogram would be written as "IИC" earlier than the 17th century.

The removal of the second layer of paint in the background and on the borders was made by softening it with the aid of cotton wads wetted in an organic solvent.

The background of the first layer is painted in whiting and is slightly glazed with auripigment. The nimbus and the borders are painted in light ochre. The letters in the monograms are of cinnabar and are small in size. Their location on the icon coincides with those in the second layer of paint. The designation of the monogram of Christ is changed to the traditional "IC" "XC". The experimental removal of the paint on the veil of the Mother of God and the Infant's tunic has revealed the existence of an intermediate layer dating back, probably, from the time of the first renovation of the icon. Christ's tunic is painted in ochre while the assist - in auripigment. The red scroll in the hands of the Infant has remained from this layer of paint. Unfortunately, the paint on the garments of the Mother of God and the Infant has remained only in fragments and, thus, the layer-by-layer clearing of paint was, in this case, not feasible, and in the course of subsequent restoration, the intermediate coat of paint was removed, simultaneously, with the upper coat which dates from the 19th century.

The first layer of paint in the background and on borders, and the coats of paint on the garments of the Mother of God and the Infant can, probably, be dated by the 14th century. This early dating is confirmed by certain formal sighs: the auripigment assist on the Infant's tunic, the red colour of the scroll, and the manner of letter-writing.

The hard paint of the first layer on the borders and the background was removed by scalpel. The background under it was found to have been removed by a broad sharp instrument which had left deep incisions in the gesso ground. At places, the layer of the remaining original gesso ground is so thin that the fabric was exposed. The fabric under the gesso ground was saturated, as was shown by the chemical analysis, in incense. On the background, along the boundary between the images of the Mother of God and the Infant, there have been found small remnants of the ancient original silver background. The fragments of the silver have been found near the right shoulder and along the left contour of the Mother of God's head and also around the Infant's head. On the silver, left of the Infant's head, remnants of the cross - thinly painted in cynnabarron the nimbus-have beeb found.

The icon bears a half-length portrait of the Mother of God. Her head is slightly turned to the right (from the viewer), her right hand before her chest. The Infant Christ sits on her left arm. Christ gives a benediction by his right hand while, in the left hand, he holds a scroll. The flesh priming on the faces of the Mother of God and the Infant is greenish, it is laid thinly, and whiting is almost absent in the colour so that one can discern the gesso ground and the dark drawing on it which was made with wide brush strokes accentuating the shape of cheeks and cheek-bones. The highlights on the faces are with wide dabs of whiting. The silhouette of the face of the Nother of God along its boundary with the cap, and the contour of the right arm of the Mother of God are shown with a broad, flexible, dark and almost black line. There remain traces of then black lines marking the contours of the veil and the Infant's head. The true images of the figures of the Mother of God and the Infant are considerably smaller in size than those on the renovation coats. The veil of the Mother of God is red-brown and dark, showing broad black lines used to accentuate the filds of the garments. Left (from the viewer), on the chest of the Mother of God there are remnants of the depiction of the stars made of precious stones: four red stones, four white stones, and one greenish stone. The edging of the veil is painted in ochre and highlights-in auripigment. The cap is green. The Infant's tunic is painted in light ochre while the assist-in auripigment. The icon has suffered badly from the impact of time and numerous renovations and has come down to us with many losses and distortions.

It was already mentioned that the ancient silver background and border had been cleared almost completely. Microfragments of silver can be detected only if the painted surface is studied

attentively. Across the entire icon, beginning from the upper border, across the face and the veil of the Mother of God there a later-made filling-in of the renovation gesso dround, dating from the 19th century, together with the temporarily extant coat of paint. Thus, there have been lost in this connection the angle of the right eye, the right side of the nose and the right side of the lips on the face of the Mother of God, the wrist of the Infant's hand giving the benediction, and the fingers of the right hand of the Mother of God. What has remained of the left hand of the Mother of God is only a fragment. As for the remaining part of her left hand, the legs of the Infant and the lower of the veil, they have been lost completely, and the coat of paint, dating from the 19th century, the time of the last renovation, which has remained on this area, lies on the fillings-in of the gesso ground of late origin. The paint on the lower border of the icon consists of fillings-in made at various times. There are traces of a burn on the veil of the Mother of God above the Infant's hand giving the benediction. The paint coat is worn out heavily. There are many small fillings-in of later gesso ground on the garments of the Mother of God and the Infant. There have been worn out and lost the fingers of the Infant's left hand and the ancient picture of the scroll. However, the extent to which the paint coat has been preserved makes it possible to form a clear idea about the artistic merits and the stylistic pequliarities of this monument.

The opened icon of "Hodegêtria" Mother of God is a most ancient one not only in Ryazan but also in the Ancient Russian art as a whole. Confirmation to this effect can be found in the way the panels were fastened together with overlaid slats, and the original silver background which occurs only on monuments dating not earlier than from the 12th-13th centuries, the green face priming, accentuation of highlights on the faces with wide whiting dabs, broad wide stripes used to show folds of the veil, auripigment assist, the presence of the fibula of precious stones instead of the star which became traditional only later.

The opened icon has a special importance for the history of painting in the ancient Ryazan. The antiquity of the image makes it possible to evoke the legend, existing in the Ryazan about the famous icon of "Hodegetria" Mother of God brought by Bishop Efrosin from Afon. The event took place before 1225 since Bishop Efrosin met a no less icon of Nikole of Zaraisk in the land of Ryazan precisely in 1225. The Hodegetria Mother of God icon was in the Assumption Cathedral in Old Ryazan. In 1237 the Tartar Mongol hordes led by Baty burnt Ryazan and "...took all the ornaments of Ryazan and the riches of its Kievsky and Chernegovskoye kinsmen while the temples of God were looted"1). The "Hodegetria" Mother of God icon remained, miraculously, intact, and when the Ryazan prince Yuri Ingorevich returned from Chernigov and learnt about the death of his son Fedor Yurievich he went to the cathedral church of the pure and glorious Assumption of the Holy Mother of God and wept profusely"2). Prince Yuri Ingorevich "... wept before the image of the Holy Mother of God of the honest and glorious Hodegetria brought in by Bishop Efrosin from the Holy Mountains"3).

If one supposes that the opened "Hodegetria" Mother of God icon was brought by Efrosin from Afon, then it can be dated with a sufficient degree not later than the 20s of the 13th century.

The "Hodegetria" Mother of God icon was an object of special veneration. The history of its renovations is connected with that of the Ryazan land itself. First, it was renovated in the 14th century in the period when the principality was ruled by the acute politician, the Great Prince Oleg Ryazansky. Second renovation was connected with the upsurge of the culture in Ryazan in the 17th century under Metropolitan Stefan Yavorsky. At the same time the system of panels fastening was remade. The horizontal overlaid slats were removed to be replaced by inset ones with additional dovetail supports. A thick layer of gesso ground was laid upon the reverse of the icon, and the "Adoration of the Cross" was painted. The third and fourth renovations relate to the second half and the end of the 19th century - the latest economic upsurge in Ryazan.

Thus, as a result of the restoration we have one more work of the pre-Mongolian period. No direct analogues among the icons in the collections of our Museums have been found yet. Probably close analogues of the icon under consideration should be sought among the Afon icons, and this is a new task for the specialists.

References

1) D.S.Lichachev. Povesti o Nikole Zaraiskom (The tales about Nicola of Zaraisk). Transactions of the Ancient Russian Literature Department, Moscow-Leningrad, 1949, VII, p. 373.

2) Ibid, p. 388.

3) Ibid, p. 373.

NATIONAL ARTISTIC HERITAGE AND ITS PLACE IN CONTEMPORARY SOCIETY (PROBLEMS OF CONSERVATION OF LATER ICON PAINTING)

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Art collectors and art lovers have in the past decade shown interest for collecting later icons and articles of religious worship. This range of movable monuments has not yet become a phenomenon capable of catching interest of experts. An opinion has been formed within a long period of time that works of later icon painting are not monuments of art. In fact heritage, tremendous in terms of quantity, preserved in working Russian orthodox churches, in old-believers' praying houses and private homes, is far from being uniform in value in terms of quality. The scepticism of museum workers erects a barrier, which is difficult to overcome, between ancient works of art and the so-called "floating" stock, i.e. later unregistered and uninvestigated monuments. Being a sequence of the ancient tradition, with the 17th century as the time boundary, the 18th-19th centuries icons, after falling into the hands of art lovers and collectors, are given all the features of earlier centuries. The ambitious aspirations of private collectors result, as a rule, in the destruction of monuments through incompetent restoration and moral devaluation in the eyes of art historians. Remaining outside the sphere of museum life, the 18th-19th centuries icons frequently become objects of operations in some cases prohibited by the Soviet law. The absence at the present time of publications which could raise the prestige of traditional icon painting results in the oblivion of very interesting and rich layer of popular culture.

A special attention paid to ancient monuments of Russian art after the Great October Socialist Revolution had certain objective reasons. The early decrees of the Soviet Government ensured first of all the identification, museofication and restoration of works of the 12th-17th centuries old Russian art. It were these works of art that made possible the formation of national art. In so doing one of the registration instructions, issued in 1949, termed as monuments works of art created before the 17th century including. The 19th century was admitted into the range of monuments only if there were signatures of outstanding artists and dating inscriptions. Thus, the exclusion of later traditional icon painting has become practically legalized.

In the post-war period it was impossible to spare time and money to identify monuments of art. It was only in the 1960s that museum expeditionary activities were activized. Again, the chief attention of experts was directed at finding ancient icons. Among the greatest findings and restoration discoveries of that period one should cite "Archangel Michael's Council", 13th century (the State Russian Museum), "Our Not of Human Making Saviour", 13th century (the State Tretyakovskaya Gallery), "Virgin Mary", 15th century (Suzdal), "Nativity", 16th century (the State Russian Museum). Such great schools of art as the Tver school were discovered. More attention began to be paid to regional stylistic groups which were composed of icons from the Novgorod provinces: Karelia, Vologda and others, more known under the contingent collective name "Northern paintings". But the traditional icon painting remained as yet outside the interests of art historians. Their rigorous judgment influenced to a considerable extent the popular collectors' activity which avoided later monuments of art. The 18th-19th centuries icons, included in rare cases in museum collections, rather stressed the general rule.

The last decade can be termed the time of the review of common and long-standing aesthetic categories, the time of the reappraisal of values. Later monuments of art have gradually bogan to be involved in the museum sphere. The exhibitions of icons in Leningrad in 1966 and Moscow in 1977 made it possible to evaluate, on individual examples, the distinctive peculiarity of later art.

In this connexion, of special significance has become the arrangement of registration of the "floating" stock in working Russian orthodox churches and old-believers praying houses. The USSR Scientific Research Centre of Restoration (VNIIR) plays an

important role in this work. Beginning from the 1970s, a group of the VNIIR experts has conducted a planned investigation of religious organizations in Moscow and its environs, in Latvia, Estonia where there were large old-believers' centres, and other places. They found unique works of art of the 15th-17th centuries. But these did not introduce innovations into the history of ancient Russian art which had already been formed. They only consolidated and enriched the commonly accepted ideas. It is owing to this fact that the VNIIR experts directed their efforts at studying later monuments of art. Their practice over many years made it possible to prepare some directive and methodological materials and publications giving general characteristics of later icon painting full of peculiarity, originality and multifacetedness. The 18th-19th centuries icons raise many problems whose solution will enrich in many ways the history of art. In so doing the researches are far from ranking together works of art of the 15th and the 19th centuries.

But we still do not have enough experience which would help make clear the understanding of the phenomenon of the later icon painting tradition. We know such great centres of icon painting as Palekh and Mstera, although there are no generalizing investigations of them available as yet. In future it will doubtlessly be possible to find some other independent centres. The exceptional productivity of numerous icon painting workshops eventually resulted in creating iconographic stereotypes, standardized artistic thinking and execution, and in simplifying the artistic language and technical methods.

While taking a retrospective view of the 18th-19th centuries icon art, we must keep in mind that after the reforms of Peter the Great icon painting, which was previously the sole and basic display of the spiritual life of the people, was given a very minor role of exclusively religious significance. The new European trends in Russian art were inaccessible and incomprehensible to Russian peasants. The icon, as an object of hopes and aspirations of the people, remained as close and necessary to them in their practical everyday life. The psychology of perception of beauty of the surrounding world was of an icon nature. Decorations and ornaments of peasants' everyday household articles were in tune with the icon tradition.

The official interior decoration of religious institutions went a different way. The transfer of the practice of European artistic outlook and the essential principles of European baroque to the Russian soil created a peculiar church painting. Individual western elements were already well-known in Russia from the mid-17th century. The first Russian theoretical treatises and the artistic work of the 17th century icon painters Iosif Vladimirov and Simon Ushakov legalized the right of the new stylistic concept to exist. The role of the prints of the famous Piscator Bible is invaluable in this respect. The turn of the 17th to 18th centuries masters Tikhon Filatiev, Kirill Ulanov and Yevtikhy Zubov continued to combine the principles of the ancient Russian icon: flatness, spiritualism and irreality, with the European understanding of proportions, perspective, volume and light and air medium. And although later artists failed to get rid fully of the traditional principles of icon painting, they still achieved a new artistic result in the sphere of new art. The most vivid and extreme example may be the iconostasis of the Cathedral of the Vvedensky Monastery, Solvychegodsk. Its icons were painted in 1693 by Stepan Narykov under the exclusive influence of the Flemmish school of art.

Professional artists who finished an academic school were for the first time in the artistic practice in Russia employed to create the interior decoration of churches during the entire 18th century. Among them we find visiting foreign masters, such as Luis Caravacc. The famous Russian artists, commonly known as creators of the school of Russian portrait in the history of art, I.J. Veshnyakov, A.P. Antropov, V.L. Borovikovsky and in the early 19th century also O.A. Kiprensky, all of them left their trace in icon painting. Some of them started with it, others did it all their life. Icon painters, whose names have become known only of late, Ivan Kirillov, Yefim Ivanov, Fyodor Leonov of Dorogobuzh, Yakov Pavlovsky and others, worked at the same time with them.

The influence of European baroque on Russian painting was imprinted on the interior decoration of the main cathedrals of the largest cities in Russia. But the lower classes of the people persisted in keeping to the traditional forms of icon painting over the entire 18th century. In the later period one

can note the growing simplification of the drawing, colour and restriction in the use of subjects. The prevalence of one-figure compositions and subjects is noticeable. The masters of Palekh and Mstera alone demonstrate their refined craftsmanship in exquisite small-size icons of the 18th and early 19th centuries. Their icons in style are patterned on the 17th century samples executed by Stroganoff's masters and masters of the Armoury.

The notorious icon painters of Suzdal begin to a large extent playing a negative role in the 19th century. Joining together in artels (icon painters' cooperatives), they organized a belt line production of icons attracting buyers by their cheapness. They were executed on poorly treated boards with inferior quality paints. The painting, covered with poorly boiled drying oil, became very soon coated with a film of reddish hue. Such icons were popularly named "reds". But samples of popular calligraphy, full of charm and ingenuousness, can be found even among them. In the event when icons were to be encased in metal frameworks, icon painters, sparing themselves trouble, painted only faces of saints which subsequently remained uncovered. Perhaps, it was these icons that were described by the popular proverb: "When not worth praying to, they are still good to cover pots with".

A special role in the 19th century Russian icon painting should be assigned to the Academy of Arts with its orientation to Raphael and the Bologna school. Numerous copies and prints of masterpieces by great artists, brought by the scholars of the Academy back from Italy, made them accessible to the widest circles of art lovers. The most wellknown subjects entered Russian iconography. Particularly popular became "Our Lady in the Armchair" and "Archangel Michael" by Raphael, "Christ in a Crown of Thorns" and "Joseph with Baby Christ in His Arms" by Guido Reni, "Baby John the Baptist" by Murillo and others. And the picture "Praying for the Cup", painted by the Russian academician F.A. Bruni in 1834, became the source of numerous versions which filled the interiors of Russian orthodox churches.

The academicism in painting inspired also the appearance of "academicism" in icon painting. Large icons, executed in the traditional form, amazed one with the dryness of the drawing and excessive use of gold in the decoration of clothes and in backgrounds. The irrational attitude to gold in ancient time as an "image of light" was superceded in the second half of the 19th century by the demonstration of rich beauty.

Elements of external fine appearance and emphasized decorativeness begin playing a greater role in the second half of the 19th century. Eclecticism in various spheres of artistic activity acquired in icon painting peculiar forms of neo-Byzantine and pseudonational character. Motley ornamental motifs thickly cover icon margins, imitating the colour effects of bright precious stones and enamels.

Old-believers' workshops became more active at the turn of the 19th to 20th century, producing magnificently executed icons in the 17th century style and preserving the technological processes of the time. They achieved an exceptional accuracy in their stylizations, thus making contemporary attribution extremely difficult.

This brief outline of the 18th-19th centuries icon painting is necessary in order to understand the material which is at present an object of an investigation in working churches and old-believers' praying houses. Numerous stylistic strata, brought about by objective historic reasons, among countless stereotype works, make possible finding outstanding monuments capable of taking their place in a museum exposition and producing not only historic and documentary evidence of traditional icon painting, but also aesthetic and emotional impressions.

The purchasing commission of the USSR Ministry of Culture recommends museums, when adding to their collections, to pay a serious attention to the characteristic samples of traditional painting. The inclusion of the 18th-19th centuries icons in the exposition of the Moscow Regional Museum of Local Lore in Istra can be cited as a positive example. The exhibition of new entries into the Andrei Rublev Museum of Old Russian Art, opened in 1983, included a great number of later works of art. But this has not yet become a rule, with the question of registration and subsequent museofication remaining open.

One of the weak spots in the registration, fixation and study of later icons is the organization of investigation of churches.

With a large number of the latter and shortage of experts in this specific sphere it does not seem possible to carry out this colossal work within a short period of time. Negative consequences in the meantime, unfortunately, occur. The theft of icons from churches and private collections and their subsequent smuggling out of the USSR cannot but cause grave damage to the national heritage. The appearance of illegally smuggled out icons at international auctions creats an equivocal prestige for their organizers. Possibly, this problem should be paid more attention to within the framework of the ICOM.

It can be reiterated that the icon continues playing its fairly considerable role in contemporary society. Without outlining its time boundaries and leaving aside its religious significance, we shall note that it affects the broadest circles of art lovers irrespective of their professional duties. The icon will have become by the end of the 20th century a social phenomenon capable of exerting a serious influence on the formation of tastes of society, its ethics, fashions and prestige. The negative aspects of this process take such forms which cause an irreparable moral and material damage to this country. Unsettled legal relations between various state and local authorities and the church make difficult in many ways a correct organization of the registration of religious monuments.

Registration as the primary form of the investigation of later monuments of art cannot yet now produce final results. We are still on the threshold of solving this problem. But along with the ever expanding role of the registration of movable monuments the problem arises of working out the principles of attribution and museofication.

In spite of the many difficulties of the problems that were touched upon, the process of the fixation of works of art has in recent years acquired a more purposeful nature. An automatic information system "Monument", which will also be used to process the material we are interested in, is at present being set up within the framework of the USSR "Law of Protection and Use of Monuments of History and Culture" and with the support of the USSR Ministry of Culture.

SUMMARY

The examination of a particular group of icon boards allowed the researchers to establish their common origin, their dimensional and other characteristics, to learn more about ancient crafts, glues, preferences for construction types and methods, storage conditions and so on. Besides in was possible to detect the gradual changes in the development of technology, as well as in the individual manners of icon boards preparation. It seems that in the Vth century every icon painter had prepared icon boards by himself, thereas later this situation was considerably modified. Boards were cut and glued by other persons, not by artists. So the ancient icon boards serve as important monuments of material culture and reflect age-old traditions of Russian craftsmanship.

EXPERIENCE OF INVESTIGATING ICON BOARDS FROM THE ICONOSTASIS OF THE ASSUMPTION CATHEDRAL AT THE 1497 CYRILLO-BYELOZERSKI MONASTERY

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Herein there were investigated 56 boards of icons: fully the deijesus row - 21 icons (190 by 80 cm. average dimension), the festival row - 24 icons (84 by 62 cm. average dimension), 8 (out of 9) boards of the prophets' icons of varied dimensions. The investigated icons, except for three festival ones, were painted on linden boards. The deijesus icons consist, as a rule, of three parts (16 icons), the central icon - of four, 2 icons - of two parts, and the last 2 narrow icons - of one board. 20 festival icons are made of two parts, 4 icons - of three parts. The prophets' icons are of two (3 icons) and three parts (5 icons). Approximately half the boards are 30-40 cm. wide, the other half, 20-30 cm. wide. In all icons only four boards are 40-43 cm. wide. Several icons are added to each on one end narrower boards, 3-17 cm. wide. Two narrow (15 cm.) boards are glued into the middle of the two archangels' icons. In olden time boards kept the dimension of the tree trunk; they were broader on one end, and narrower on the other, the difference can be 2-4 cm. Boards were glued together by joining the narrower end of one board to the broader end of another one. The most popular one were 20-40 cm. wide boards, this, possibly, reflected the dimensions of ripe linden timber. Several icons are distinct in their design. In the local row one icon consists of four parts, and besides, a part of the upper, lower and right-hand margins are superposed; about 0.8 cm. wide boards are glued on to the main board. These are not subsequent repairs, but the original design, since all the parts are under a whole piece of fabric glued on to the board (stretched over) and staying under the prime coating. This gives rise to a presumption that boards for icons were made in the monastery itself of seasoned wood which was in short supply. The master, fearing cracks, removed the central (nuclear) part of a wide board in a local icon and inserted a narrow board instead, fastening it with the main boards in several spots with carefully cut out and glued-in wooden inserts (from 6 to 3 cm.). One of the festival icons is shorter than the others by about 4-5 cm. This is not a subsequent re-making either, it was the original dimension of the icon, which also shows an extreme economy of wood when executing icons.

The three festival icons ("The Weeping", "The Persuasion of Thomas", "The Washing of Feet") are distinct in their design: each of them consists of a wide pine board (54, 54 and 53.5 cm. respectively), to which two narrow linden blocks (8 and 3.5 cm.) are glued in the first icon, one block (11 and 12 cm.) to the second one third one each. Obviously, one and the same pine board was used for the three icons, its nuclear part in the middle is cracked identically in all the icons, crackle is developed in these spots on the face of the icon, the prime coating has losses on the border line where wood of different species was joined together. Different species of wood were glued together only in the three above-said icons out of the entire iconostasis. The masters also avoided taking boards from the very centre of the trunk so that the nucleus might not get in; even, as we saw above, removed it to preclude cracks on the icon face both in the prime and painting coats. The centre itself was dangerous, and there were very many, if not the majority, boards situated close to the nucleus. Such boards were glued together in olden time in a different way than by modern masters, - the nuclear parts of the neighbouring boards face one way. Modern masters are wary of glueing boards together in this way, so as not to cause warping of the glued boards, and make the nuclear parts face the other way. Modern methods of glueing boards together reflect another stage of the handicraft tradition, when less seasoned wood began to be used. The central parts of the 17th century icon boards face the other way, - "in a modern manner". Old masters did not follow that rule.

The traces of treatment, remaining on boards, make it possible to reconstruct some methods of treatment unknown to us. Boards were cut out of a log first roughly, carelessly, with uneven notches made with very sharp axes. Boards were seasoned in this roughly cut form. In so doing, they had some sort of additional

treatment: Dark spots, looking like traces of burning, remained in axe-cut notches on many investigated boards. Such dark spots were found on icon boards from other 15-18th centuries iconostases originating from various regions. It is known that the 15th century German masters burnt tree trunks, chosen for executing sculpture, with a view to drying them, adding strenth and preventing biodecay[1]. A supposition arose that Russian masters also employed a similar method for icon boards. However, it became clear in the course of investigation that it was not burning, nor impregnation, but traces of some surface coating. Its composition has as yet not been determined, but is under investigation. It is possible that this coating was of an interim conservation nature, because the black surface coating was fully removed during the subsequent final treatment of the glued boards, remaining accidentally only in some notches. Roughly hewn boards were glued together and then cut finally with a sharp tool (scraper or knife plane) with a 2 cm. cutting surface, leaving shallow grooves. On the back of some boards they are horizontal, on the others, vertical; part of the boards were cut so smoothly that the direction of cutting can be determined by means of fleeting lighting. The face sides of the boards were cut so smooth that they have no notches.

The upper and lower margins on the deijesus icons are on the average 7 cm., side margins, 6 cm., and those on the festival ones 6 and 5 cm. respectively. The prophets'icons have no margins. Margins were cut from the inner to outer edge on all sides, i.e. they are 0.5 cm. thinner on the icon edge. Each icon has two counter (not through) keys. A trapeze-like slot was cut to the half depth of the board - 1.5 cm., for them. Key slots are not parallel, but come close (2-3 cm.) together at one end. The blocks are also trapeze-shaped and were pressed into slots with great force. The keys, which came out after some time, have dents noticeable on their sides. The keys acquired the final shape after they had been inserted into icon slots. The keys in the boards were most often pine wood. In all deijesus icons keys were pressed in at about the same distance (120 cm. on the average) from one another. In the festival icons the distances between keys differ: in some icons thay are at a distance of 50 cm. from one another, in others, 36-40 cm. In order to have an additional fastening of icons in the iconostasis the icon keys have holes drilled in them, in which raw leather belts were inserted, tied with the same knot, and which are details of the original design of the 15th century icon boards.

Besides common methods of making icon boards, there are a number of design features peculiar to individual groups.

11 icons of the deijesus row have linden keys with carefully cut off ribs on all sides, the traces of the finishing of the boards are horizontal.

Other 8 icons have pinewood keys of rather a rough shape, ribs are not cut off, projections are cut off under a right angle, the back is bevelled, the finishing traces on the boards are vertical, often hardly noticeable. The festival icon boards hav even more distinctions. Nine boards are thinner and lighter tha the others, the finishing traces are horizontal, all the keys are lindenwood, all the upper keys were pressed in from right t left, at about the same distance (50 cm. on the average) from the lower ones, key ribs are cut off on all sides, have no hole drilled in them, raw leather loops are nailed to the upper edge of the boards. Nine other boards have not linden, but pinewood keys, the direction of the upper one is not as stable as in the first group, they were pressed in both right to left, and from left to right, but the distances between them in these boards are less (38-42 cm. on the average). The ribs of the keys are not cut off, some of them are roughly made, cut off under a right angle, projections and back ends are uneven, the keys hav holes drilled in them, into which knotted leather loops are inserted, the vertical finishing traces are prevalent in the boards. Three boards in this group are composed of different species. The boards of five more icons are close to the first group, but have some distinctions - they are all thicker, therefore, the upper edge of each board is hewn all over its width. When investigating odd icons, many methods of treatment and traces seem insignificant, so we omit, or pass them unnoticed. Whe investigating the whole iconostasis, the examination of boards

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1) Dieter Ecstein. Holzbiologische Untersuchungen und werktechnische Beobachtungen am Triumphkreuz im Lübeker Dom. Internatio nal Kolloquium zum Werk des Bernt Notke. Lübek 22-24 September 1976 j. S. 95-99.

can produce material suitable for attribution. The peculiarities of the treatment and making of boards are grouped within the 1497 complex not arbitrarily, but are divided into three groups which differ from one another by paints and painting methods, i.e. by belonging to different masters. It can be concluded that different masters prepared boards for each artist. It cannot be ruled out that every icon-painter prepared boards for himself. The paint is that some methods of designing boards, the quality of their making are associated with general ideas of each of the artists, produced on the basis of studying all aspects of works of art. Thus, the master who painted icons on the boards of the second group has a way of neglecting somewhat the technical aspect of the work. This can be seen in how he glues the fabric on to the board under the prime coating, the paints in his icons show more damage, and if to continue citing these examples, it can be noted that in this group of boards we can see cases of joining together different species of wood in the same icon, carelessly made keys, the employment of pinewood boards, which other artists do not have. The master of the icons on the boards of the first group (nine icons) has high technical craftsmanship at all stages of the work, an especially high quality of the work, and the boards of his icons are thin, light, and the keys are amazingly finely made.

If boards for icon-painters had been prepared by one or several masters on order from the monastery, or an icon-painters' artel (association) independently of the artists, they would have been distributed among the masters rather at random. The 1497 iconostasis displays an obvious regularity: boards with identical features of the design are concentrated with one master, the boards of another master have, with rare exceptions, other distinctions. Thus, either each artist had his "own" master making boards for him, or, more likely, each icon-painter prepared them for himself. In this way we obtain new material on the organization of labour at a 15th century icon-painters' artel (association), which cannot be discovered in any other way.

On the reverse side of icons there are various marks: notches on the upper and lower keys, punctures, scratched letter notations of figures, figures written in words, hatches, etc. When comparing marks to one another an idea appeared that the earliest of them were notches on the keys and letter notations of the figures. It looks most likely that the marks indicate the place of the icons in the row, also during rearrangements and repairs of the iconostasis; consequently, one system is superimposed on another. Best of all these marks agree on the icons of the prophets' tier which consisted originally of nine icons: in the central board of the prophets' row the key has five notches and at the top of the board the letter "e" - "5" is scratched, i.e. the icon was the middle one, the fifth in succession; there are nine notches on the icon on the extreme right, the ninth, if to count from left to right.

When comparing notches on the festival icons another supposition appeared as to their purpose. The boards were, as we have found, made by different masters, and didn't each one mark boards made by him? Thus, in the third group the keys have two or three notches each, they are sufficiently deep and clear cut, but boards of another group also have two or three notches each (some have eight), but they are less deep and clear cut, so it is sometimes hard to decide whether it is one notch or two.

The possibilities of the investigations of monuments are unlimited. It is not only painting that is of value in icons, the 15th century boards are in themselves monuments of material culture, the way they were designed and treated reflects age-old traditions of craftsmanship which by now has stood the test of time for 500 years.

We believe it very important to organize a planned study of monuments of icon-painting in various regions by local experts in accordance with an agreed programme (boards, prime coatings, the pigment composition of the painting coat, etc.). Only by joint efforts by many specialists could it be possible to do the work on the systematization and generalization of odd pieces of concrete material which remains virtually uninvestigated.

SUMMARY

would like to address this hort iconographic study first of ll to the restorers of the Old ussian painting, for such no- ions as the style and the icono- raphy are not only a scientific atagories, but a practical one, nd also because of the fact that n the contemporary restoration t is not possbile to determine a orrect course of the revelation f a monument without exact know- edge of its style. One of the rinciples of the many-parted cons' arrangement is considered n this article. In every par- icular case the different sub- ects allowed a master to reveal certain theological notion. he considered icon consists of wo reverses: 1) "Resurrection" nd 2) "Fiery ascension of Eli- ah the Prophet." To the right f them there is the image of the postle Peter represented in the ull length of the board. The pocalyptic matter of the two athedral epistles was known in us during the 15th century, hat's why the artist combines he two subjects with the pur- ose to indicate the "Fiery Apoc- lypsis." On the whole, in the ountries of the Near East the otions of the fiery apocalyp- ics had been formed in the an- ient Iran and then came to the hristian epoch. That is why in he article the greatest atten- ion is given to the eastern ources flowed into the old Rus- ian culture so organically.

THE NOVGORODIAN THREE-PART ICON FROM THE COLLECTION OF THE STATE TRETYAKOW GALLERY

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In the collection of the State Tretyakov Gallery there is the three-part icon with the Apostle Peter's portrayal and the image of two reverses: "Resurrection" and "Fiery ascension of Elijah the Prophet"[1] dated from the second part of the 15th century. This icon appeared among publications rarely,[2] and its contents were not subjected to a special analysis. Against the general background of the Novgorodian painting of the 15th century both the quality and the nature of its execution are not distinguished by extraordinary signs, but the selection of the subjects is not casual and is worthy of intent consideration, for the eschatological meaning of the Apostle Peters' prophesies[3] in his First and Second cathedral Epistles is discovered just in accordance with the ideas of that epoch (i.e. in the 15th century). By the prophesies it is known that the end of the world fell on the 7th millenium, i.e. on the 1492, so by the late 15th century - the early 16th century this legend "turned into the main problem of the time."[4] It is possible to judge of the breadth of these ideas' dissemination over Russian North by the following example. Thus in the tier icon with the image of the Apostle Peter (the collection of the State Russian Museum)[5] similar by the time, the style and the place of the origin to the considered monument the usual inscription on the Apostle's scroll with the recognition of Christ as the Son of Living God[6] was replaced with the words. "From the Peter's Epistle cathedral". Surely, the author of this three-part icon was conversant enough with the apocalyptic literature, but it is characteristic that his interpretation as a whole was permeated with the ideas existed not in Byzantium itself, but in its eastern provinces (Syria, Mesopotamia, Palestine, Egypt). The combination of several subjects within one composition with the purpose to connect symbolic phenomena of the Old Testament with the deeds of Christ and the apocalyptic predictions is known all over the Christian world beginning with the painting of catacombs,[7] but the fiery apocalyptics were accepted only in the eastern Christian countries, and in spite of the sizable distance these ideas have found absolute understanding in Russia. And that's why the analysis of our icon should be begun with the reverse. "The fiery ascension of Elijah the Prophet" received the absolute and the deepest philosophic comprehension just in Russian painting, and in comparison with which even such the ancient patterns as the fresco belonging to the 4th century from the catacombs of Peter and Marcelina in Rome[8] and the relief of the carved doors in S. Sabina church in Rome[9] are of illustrative character. Both in the first and in the second cases the Prophet is translated into Heaven in a chariot, and there are not attributes which point out the fact that the ascension is fiery. There are none in many European[10] and Greek[11] patterns either. But as for the Russian iconography, in all its works connected with this subject a part of the heavenly fiery element descended onto the earth and taken the Prophet inside[12] is depicted. In the eulogy on the Prophet Elijah read on July 20 the apocryphal legend according to which the Elijah's mother before his birth saw that some men in white chasubles: "created his name, and swaddled him in fire, and fire gave him to eat"[13] is cited. Undoubtedly, this legend is eastern by its nature[14] as by the eastern notions the heavenly element consists of fire. In the Book of Enoch the third day of creation is described the following way: "And all the heavenly hosts I gave the image of fiery substance, and from fire grades of incorporal hosts, their armaments are fiery, their garments are burning flame."[15] By the way, the God is pictured arrayed in red, and His blessing arm in Heaven symbolizes its fiery nature quite definitely.[16] Such an intent interest of Russian theology has almost the genetic reasons and is founded on fiery cults of Iran brought to Rus by the Skyths.[17]

The description of a funeral of a Russian by Ibn Fadlan (10th century is quite appropriate to be cited here.[18] "A man of Russians was standing by me, and I heard him talking with the translator attached to him. I asked him about what he had held the conversation and he replied, that the Russian had told him: 'You, Arabs, are foolish people, for you take the sweetest and the most honourable of men for you and abandon him inside the earth where reptiles and worms are eating him, but we do burn him in fire, and he translates into the Paradise at once! Then he burst out laughing excessively and told: "By love of his Lord (the God) to him, inficted He the wind, so that the flame will envelope him in an hour! And really, no sooner an hour has passed, the vessel, the firewood, the dead man and the maiden turned to ashes."[19]

According to the notions of the Christian East in definite cases the image of the Apostle Peter is connected with the fiery apocalyptics quite realizely. I shall list three examples. I) In the extract from the anonymous parchment manuscript found inside the Ahmim tomb in Upper Egypt in the late 19th century there are the fragments from the New Testament by Peter and the Apocalypsis by Enoch. II) The Georgian fresco dated from the 11th century in the western apse of the Atenian Sion[20] where the Apostle Peter bringing the righteous to the Gates of Paradise is depicted. In this case all of the images are personified,

and all of them are the martyrs who died in fire: Eustace Plakida (Sept. 20),[21] his wife Feopista, his sons Agapy and Feopist and three youths in priestly garments (Hananiah, Azariah and Mishael)[22] thrown into furnace by the tzar. III) The Strogonov icon of the 17th century "Renovation of Church" from the Blagoveschensky Cathedral in Solvytchegodsk[23] where the Apostle Peter is depicted crucified with his head down, and at the pedestal of the cross as the symbol of the sacrifice there is the head of calf in flame and the inscription: "Burnt sacrifice."

Here it is necessary to return once more to the Georgian fresco where, besides the Apostle Peter and the fire martyrs who are already in the Paradise amidst the Paradise trees, there portrayed Elijah the Prophet, the Prophet Enoch[24] and John the Theologian; all of them had no earthly death,[25] and everybody was bound up with the fiery eschatology.[26]

But let us continue the analysis of the icon. The next reverse is "Resurrection" keeping the second position not as a subordinate, but as the main in this structure, and with respect to it "Fiery ascension of Elijah the Prophet" has only the explanatory meaning indicating the way to Salvation through fire and martyrdom. I shall adduce the two quotations. The first of them is from the ancient text "Zend-Avesta": "At the end of the World there will be the resurrection of deads, Ahriman is being conquered, there happens the fire clearing the world and abolishing the sin".[27] And the second one is from The Second Epistle by the Apostle Peter: V.10 - "The Day of the Lord will come like a thief, and then with a roar the sky will vanish, the elements will catch fire and fall apart, the earth and all that it contains will be burnt up." And V.13 - "What we are waiting for is what be promised: the new heavens and new earth, the place where righteousness will be at home."

The loss of "Resurrection" in this icon is quite usual.[28] In the centre of it, within the round three-colored mandorla arrayed in shining garments Christ stands treading under feet the broken Gates of the Hades. His figure turned to the right. In His left hand He holds the big black cross, by His right hand He raises Adam from the coffin. Above Adam there is the group of the Saints - Eve, John the Baptist, Stephen the protomartyr. In the left group there are the Prophets David and Solomon raised from the coffin. The location of the NT protomartyr Stephen instead of the OT protomartyr Abel is unusual for that time. The garments of Stephen, the white tunic with the maniaky (shoulder-piece), permits to assume exactly his image, while Abel wears the same white

cloth and has a pastoral staff in his hands. However, in the fresco belonging to the 14th century in Kahriye-Gamii[29] in the reverse "Descent into Hades" Abel wears the same white tunic, but he holds a staff there. This figure has no staff in our icon. It's possible to add here one more detail which indicated the penetration of the eastern Christian iconography into the Novgorodian painting. Thus in the four cave-churchs of Sabeareby where the painting of the 8th-10th centuries es executed in the Syrian-Mesopotamian traditions the image of Stephen is without fail and usually placed in front of an altar apse or in front of a Cross.

It is possible to attribute the manner to show the infernal flame as the two-coloured segment under the Gates of the Hades to the Unusual details of the reverse "Resurrection" in our three-part icon. As a rule, fire is not painted in this subject at all. And only in the two Pscovian icons belonging to the 14th-15th centuries it was painted in the form of the yellow semicircles framing the entry to the cave.[30]

And once more about the image of the Apostle Peter in the three-part icon. In spite of the fact that he is standing next to the Resurrection he has no keys in his hands. But in his left hand there is the scroll with the word "otveshchaet" ("Replys"), i.e. with the same quotation he appears before Christ in deesis cycle as before the Heavenly Judge though the figure here is not in three-fourth as it is in deesis, but in full face. Proceeding from the assumption that the master of the icon for all his professionalism was a sufficiently plebeian person it's possible to conclude that the above-stated ideas on the essence of the Resurrection known all over the eastern Christian world existed here, i.e. in the North of Russia in the great mass of the population. Surely, that could be the client who has dictated the arrangement of the reverses, but this does not change the matter. As it was already told, the theme of the fiery apocalyptics had accustomed organically in the Ancient Rus beginning with the ancient times till the 17th century including. And if from these positions to consider not only the iconography "Fiery ascension of the Prophet Elijah", but the other subjects connected with the "fiery" theme it will be possible to trace the genetic links with the culture of the East, and sufficient self-dependency the same time, and definite profundity of the philosophic notions in the interpretation of these ideas.

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4. Sakharov, V. Eschatologic works and legends in the old Russian language and their influence on popular spiritual verses. Tula, 1879, p. 62.

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6. Mt. 16,16; Jn. 6,69.

7. The combination of the subjects also indicated the hierarchical co-ordination of the appearances leading to the Salvation and the eternal life. Already in the 3th century the reverses "Daniel in the Lion's Den" and "Raising of Lazarus" reminded the Christians of the future Resurrection in the catacombs of Domitila. - See: Frikken, A. von: Roman catacombs and monuments of early Christian art. Moscow, 1880, v. III, p. 117, ill. 7. Later an ensemble of cathedral paintings itself would be arranged in such an order which is able to be compared with the structure of a crystal when all the facets forming it are seen through its every facet. And it is doubtful whether to be a strained interpretation the indication of the fact that in Tzargrad in the times of Lev Mankel (457-474) the Our Lady cathedral-crystal was built. - See: Serge, archbishop. The complete breviary of the East. Vladimir, 1901, v. II, suppl. II, p. 54.

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11. For instance, the miniature dated from the 11th century from The Book of Kings (The Vatican Libr., cod. gr. 333) and the Greek icon dated from the

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12. By the Book of Yashar, Enoch is translated into Heaven in a fire chariot. See: Sokolov, M.I. The Slavonic book by Enoch the righteous. Moscow, 1910, p. II, p. 164.

13. Cit. by: Smirnova, E.S., Laurina, V.C. and Gordienko, E.A. Ibid, p. 223.

14. On the ascension of Elijah the Prophet see: 4 Kings 2, 11-13. By the way, in the Bible the fiery cloud depicted in Russian icons is not described, but the fiery steeds and the fiery chariot (in Greek icons both the steeds and the chariot are red, but without the cloud). And moreover - see: 3 Kings 19. 11-12.

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19. "The custom of cremation is a heritage of the ancient Indo-European period." See: Niderle, L.: Slav antiquities. Moscow, 1956, p. 205-209. See also: Prokhorov, V.: Materials on the history of Russian wears. S. Petersbourg, 1881, p. 28, 29: "Before the Christianity the Slavs used to burne their deads."

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21. Plakida is a Roman name, when christened he was named Eustace. In the times of Emperor Adrian Eustace and his wife were burned inside the copper pier.

22. Dan. 3, 12-29.

23. Inv. CM-540-Ж; 195x59, 2.

24. According to Nicodemus (ch. 25-26) the righteous are met behind the Paradise Gates by the noble robber and the Prophets Enoch and Elijah who live in the Paradise in the expectation of the coming of the Antichrist in order to fight against him, to be executed in Jerusalem and then ascended to Heaven three days afterward. By the way, the images of Enoch and Elijah in reverses of the Last Judgement are known only by the Russian icons dated from the 17th - 18th centuries, except this fresco.

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UMMARY

THE 17TH CENTURY ICON "MOTHER OF GOD OF SMOLENSK" REDISCOVERED

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zech born, Amsterdam based, uzana Skalova is an art istorian specializing in he conservation of icons. he was trained at the stituto Centrale del estauro in Rome nd various icon museums in reece and Russia.
n 1983 and 1985 she spent 1 months as a scholarship-older at the All-Union cientific Institute of estoration (VNIIR) in oscow.
he article deals with her estoration of the 17th entury "Mother of God of molensk" which she comple-ed in 1981.
n describing the condition f the icon and the measures aken to restore it according to the wishes of he private owner- "to its ormer glory," the author ives an insight into the istory both of icons them-elves and their restoration n various countries.

Introduction

Icons are important devotional objects in the Eastern Christian rite, arguably the most important. To the faithful the frame of an icon is a window through which can be glimpsed the image of Christ, His Blessed Mother, or a favorite saint.

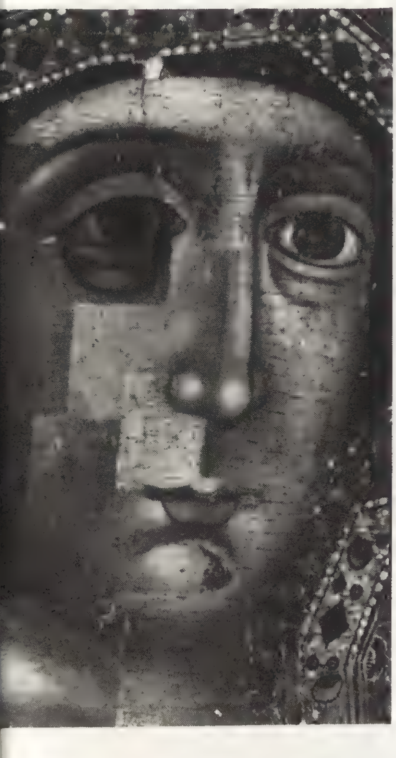
Whilst the icon endures spiritually, the materials used make its actual fabric highly vulnerable. Changes in temperature and humidity cause the wood to expand, contract, and split; central heating encourages the process of the ages.

For centuries an icon might hang on a damp wall, cold behind and warm before, collecting, after fifty years or so, a rich black coating from candles and oil lamps: hence the nickname cornyje doski -black boards. The painted surface applied to a thin ground of chalk and glue fought a losing battle against the expanding and contracting wood; it burst, chipped, or became mildewed. In an effort to counter this process the medieval artist was careful to select the correct variety of wood and reinforced the ground with a layer of linen.

The gradual decline in the art of icon painting brought with it less painstaking techniques; hence, post 16th century icons are often in a worse state than much older works. And the adoring faithful were themselves unconscious iconoclasts. Their devotions were far from gentle. They kissed their icons; they rubbed and stroked them; they scraped pieces from icons with miraculous reputations. Come snow, come wind, come blistering sun, icons were carried in procession; indeed, some were permanently exposed to the elements above the entrance to the church, home, or at crossroads. Metal decorations nailed on by grateful donors left further stigmata. Each of these varieties of damage can be compared to a disease which must be treated without wounding the surrounding tissue.

Fig: 1. Detail of over-painted layers during cleaning.

Photographs: Ferry Herrebrug Amsterdam, The Netherlands



The History of the Restoration of Icons

No seriously damaged icon was ever consigned to the scrap-heap; an icon was - is - intrinsically holy. Such icons were freshened up. The would-be restorers were usually monks. The materials with which they tried to clean the blackened olifa-varnish make grisly reading: soap and water, shellac, and even lye. Whenever possible they preferred to repaint the icon, sometimes applying a new chalk ground (1). Modern techniques allow the restorer to separate such layers. All too frequently, however, the repainting occurred directly onto the old layer of varnish, and many icons bear new layer upon new layer.

The painting of a new image over the old cannot always be explained by desire to correct damage or by lack of funds. The process of repainting with an identical image must have had symbolic and sacred overtones (2).

The more celebrated icons, those with miraculous powers, were often restored, or, as inscriptions on the icons themselves have it, "renewed." Thus, ironically, we often know the name of the restorer but not that of the original artist whose work was almost always performed anonymously.

In the Moscow of the 16th and 17th centuries there appears to have been a veritable cult of overpainting. The patriarch, the czar, and the hoi polloi enthusiastically celebrated each restoration with processions to new churches where copies of the renewed masterpieces were installed with much pomp and ceremony (3).

In the 19th century the world discovered icons as works of art *per se*. They began to appear on the market, and their holiness became a secondary factor. The restorers, still primarily icon painters, bowed to public demand. Restoration work was subordinate to the influence of fashion, trend, and collectors' taste. At first blackened, damaged pieces were in demand; later, following successful cleanings, the art world, dazzled by the brilliant colors so

Fig. 2: The icon "Mother of God of Smolensk," 108 x 72 cm, before cleaning.

Fig. 3: The icon restored.

typical of the middle ages, made over-cleaning the order of the day.

Next followed the phenomenon of the "white backgrounds," the denuded preparation layer, less damaged gilding or paint. Icons in their original state rarely have white backgrounds. It is essential that the modern restorer of icons is familiar with the history of his craft, for no icon survives a hundred years without tampering (4). Restoration almost inevitably means restoring previous restoration work.

The authorities were aware of the situation. By the end of the last century the art of icon-painting, neglected for centuries, was as good as defunct. The cultivated Slavophiles saw something uniquely Russian in danger of disappearing and took action (5). The study of icons in Russia became a science and the technique of icon-painting and renewing a part of the discipline.

In the years following 1917 Revolution the new regime confiscated church property. Many icons, also those from private collections, were gathered together in museums. Ironically an atheist state has become the focal-point for the scientific study of icons.
Igor Grabar was the driving force which gave restoration of icons its scientific basis. Under his supervision masterpieces were again cleaned in the newly founded State Ateliers. At first work was confined to cleaning and conserving with the aim of exposing the original paintwork. Retouching was taboo, this in reaction to the simultaneous improvement and obscuring, often even mutilation, which had previously rejoiced under the name of restoration.

From 1918 onward Grabar organized exhibitions of these newly "discovered" icons. In 1920, for the first time in centuries the public was able to see the 15th century "Holy Trinity" just as it had been painted by the monk Andrei Rublev, a name with as much significance as Giotto in Italy. Grabar's pioneering work continues; thanks to it we are able to reconstruct the history of Russian and Byzantine icon painting. It is not an exaggeration to say that Russian medieval icons have been the most important European art-historical discovery of the 20th century.

Theory

But the scientific approach brought with it fresh dilemmas. In times past the icon was simply overpainted in the fashion of the day by an often mediocre artist. Until quite recently the restorer influenced by the art historian, delved for the oldest layer, and all that went before was removed. Now, however, the approach is more thrifty: no matter how many overpaintings and restorations, the top layer - if it be a rare example of top quality work from a later period - is chosen.

Today, the restorer has, generally speaking, three choices: conservation and cleaning with no additions; in the case of gross damage, the filling of holes and gaps with a new chalk layer to be retouched with a clearly visible technique; and, lastly, to reconstruct damaged areas, a solution often defended by museum curators who must take account of a viewing public whose understanding of the subject is less than sophisticated. Nor do church authorities regard gaping holes as sacrosanct; damage must not be allowed to disturb the devotions of the faithful.

The most practical solutions are often combinations of the various approaches: the fragmentary cleaning of the overpainted damaged areas and/or the adaptation of previous restorations, e.g., sanding off of overpaint and giving the preparation layer a neutral tint. So complex is the question that in 1970, in Moscow, the All Union Scientific Institute of Restoration (VNIIR) devoted an entire conference to it; every paper advocated a different approach (6).

As the restorer worth his or her salt knows, every icon brings individual and specific problems; solutions depend on the quality of the painting, the format of the piece, or the semiotic value of the damaged detail.

Semiotics, the study of the system of signs, helps us to understand the significance an icon enjoyed in its hey-day. For the Orthodox, for example, the Christ Child is more important than the Virgin who bears Him in Her arms; and, thus, damage to His image was all the more lamentable. Paradoxically, the primary source of devotion was precisely that most often mutilated by adoring fingers and worshiping kisses, and hence in need of regular replacement.

Fig: 4. Sketch of damaged areas:

Holes in preparation layer

New ground & over-paint (see X-ray photo)

Areas of missing translucent painting

Wood replaced

Icons are painted in accordance with strict principles in a carefully balanced composition of colour fields. Damage swiftly destroys the icon's two-dimensionality and harmony.

Practice

Armed with theoretical data we can now approach the icon in question: the monumental 17th century "Mother of God of Smolensk" (Hodegitria variation), measuring 108 x 72 cm. How such a large church icon from an iconostasis came into private hands is unknown. Suprisingly both Russian and Greek specialists claim the icon for their patrimonium. Having no point of reference I dare not attribute the cleaned icon. It may well be the first of its type to have been rediscovered. Was it painted on Mont Athos, the meeting place of Greek and Slav influences, or in the cosmopolitan ateliers of the czar in Moscow? Or by a yet unknown painter from Jaroslavl? Frankly, I do not know.

Theory is splendid, of course; now to see how it stands the test of reality. Quite clearly, the icon has been overpainted more than once - the last time in the 19th century - not so badly either, though with a certain lack of feeling. Notice the hands in the original photograph (Fig: 2).

The fact of complete overpainting is a warning that the layer beneath is damaged. In such cases it is often wiser to leave well enough alone. But the new paint layers were of different mediums (oils on two layers of egg-tempera) applied through the centuries, one upon the other to camouflage a variety of damage: holes, cracks, and blisters which combine to hinder the conservation of the whole (Fig: 1).

In consultation with the owner (7) it was decided to work on the original, and, inch by inch, to remove the top coat. The (colour) photographs showing this operation are not only important as documentation but also give a unique insight into the artistic and restoration history of the icon. The task took 450 hours.

The splendid original painting was reward enough for the effort but the Christ Child posed considerable problems. His apparel was originally gold covered with a translucent red resin-varnish. This had been scratched off, perhaps by the pious in search of a sacred souvenir. Later, in the 19th century, the remnants, together with the ground, had been removed and the whole repainted. X-ray photographs showed a different pattern of cracks, confirming that the preparation (ground) was completely new; of the original, only miniscule fragments remained (Fig. 4. and Fig. 5).

The coarse overpainting clashed with the rest of the cleaned icon. And thus the question: what is scientifically, artistically, and morally correct action to take? To leave an older though uglier and clashing restoration which is part of the icon's history or to in-paint in more close style with transparent water-color on a ground which is not original?

The icon restorer, here in the west, must dread such decisions. Whereas colleages in the Orthodox countries work in icon museums or Institutes, with all their facilities, with the support and advice of a team, not so the westener.

On this occasion I was obliged by the owner to opt for the aesthetic approach and match the Infant to His pristine Mother; retouching offends the eye less than damage (Fig: 3).

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On the next page:

Fig:. 5. X-ray photograph, a fragment (see Fig: 4.) showing different patterns of cracks.
Photo: Ernst Klusman, Courtesy of the Central Research Laboratory for Objects of Art and Science, Amsterdam, The Netherlands.

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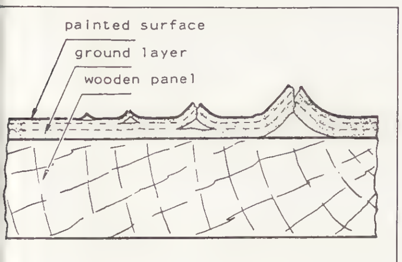
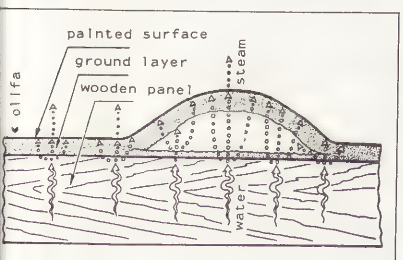
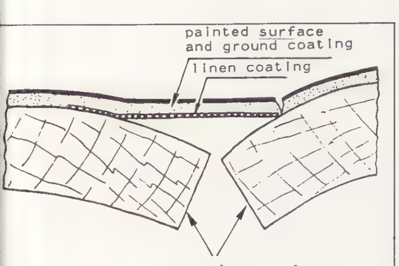


laky, cracked ground layer nd painted surface caused y dampness and subsequent rying-out.



iagram indicating formation f air bubbles in the ground ayer. This type of damage s characteristic of icons hich were hung on a damp all while being subjected o heat from burning candles nd oil lamps - from the oreground.



he flaking and cracking of oth painted surface and round coating due to arping or severing of the oints of supporting panel because of temperature hanges and dampness. The inen coating keeps the icon ogether.

SUMMARY

This paper compares the methods of depicting a human face according, to Hermeneia a post-Byzantine Painters' Guide, and icons of the XIV-XVth centuries from the Deesis Row of the Annunciation Cathedral of the Moscow Kremlin. Out of the nine icons in the Deesis only six were painted by Theophanus the Greek himself while the rest were made by his assistants. The Herminia instructions coincide completely with the technique of the faces in the six icons. It is probable that the Hermeneia Painters' Guide has been finalized as a result of canonization of the techniques of Paleologus painting. This is an indication of the time of origin of the sources of the Athon book.

HERMENEIA BY DIONYSIOS OF FOURNA AND THE ICON-PAINTING TECHNIQUE OF THEOPHANUS THE GREEK

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Comparison of the technique of medieval art with that described in painters' manuals has allowed interesting conclusions.

This paper discusses the methods of painting faces in the icons of the Deesis Row of the Annunciation Cathedral of the Moscow Kremlin.

In the six icons of the Deesis which the author attributes to Theophanus the Greek, the painter who came to Russia from Byzantium in the second half of the XIVth century, the Savior, Our Lady, John the Baptist, Archangel Gabriel, Apostle Paul, and John the Chrysostom, the technique of face painting coincides with Hermeneia's recommendations. This fact gives an impetus to a closer study of the manual.

The manuscript in its present-day form is thought to be written in 1701-1733 and 1745. However, the Painters' Guide, as Marcel Restle has remarked, is a compilation of earlier texts which in turn were based on still earlier sources. The true age of the sources of this guidebook is very important. In this context, the point of view of Henrick Brokhauz who explored the Athon monastery is very interesting. He claims that the manuscript was written circa 1300, as suggested by the iconographic schemes in the first part of the book. On the other hand, taking into consideration the language of the manuscript, he ascribes its appearance to the post-Byzantine period, between 1500 and 1630.

M. Restle has combined a profound philological analysis of Hermeneia's text with a study of a large number of mural samples in Asia Minor. The comparative study allows the following conclusions:

1. Hermeneia gives a simplified and schematized picture which by no means reflects the large capabilities of Byzantine art.

2. Hermeneia does not give a detailed and exact description of ancient techniques but canonizes a unified. The ancient methods are not presented as a separate section; they are referred to when used in later-time techniques.

3. Hermeneia contains linguistic and technical elements of the Byzantine and even Roman times; but on the whole it depicts the painting technique of the post-Byzantine period normally used by icon-painters in the XV-XVIth through the XVIIIth centuries.

In a word, M. Restle took Hermeneia to be a document of a certain time and place associated with fine arts in Athon. The scientist did not concentrate on the techniques of face-painting in Hermeneia whose text gives enough evidence to maintain that Hermeneia presented a certain stage in the development of painting technique which Athon painters inherited from an earlier school. Hermeneia's text is actually a canonization of the techniques of Paleologus art - this is indicated by the fact that Dionysios of Fourna regularly refers to Manuil Panceline, the artist who painted the Protat Church in the Athon monastery in early XIVth century, as shown by H. Millet and later by A. Xyngopulos.

The description of the order for completion of the human face in the icon suggests that it is a multilayered technique. The face is made of seven layers of different tones, with some layers being applied in several touches. The first layer - proplasmos or an overall ground color, the second layer - glycasmos or a darker flesh color, and the third layer - sarka or a flesh color - form the principal layers. They are followed by the reddish color on the lips and cheeks, a lighter flesh color, white highlights and a shadow gaze. Hermeneia instructions are to have each color made according to a specific recipe. For instance, the base layer is made of a mixture of equal quantities of green, yellow and white colors plus one fourth of the black color; this produces a green mixture with a greyish shade. The flesh color is a bright-pink mixture consisting of equal quantities of the white color, ocher, and vermilion. The second (fusing) layer is a mixture of equal quantities of the base layer and the flesh color, i.e. a yellowish-pink mixture. The reddish bloom is of red-orange color because it is a mixture of vermilion and the

flesh color while the shadow glaze is of red-brown color because it is made of bolus. The face outline is drawn by the dark-brown or greenish-brown (umber pigment) pigment and sometimes refined by the black pigment.

Hermeneia specifies not only the composition of the above mixtures but also the order in which they are to be applied. The icon-painter models the face through 12 stages each of which is associated with a certain color. First of all, he applies the ground of base color, then he draws the facial features using two colors, then applies the fusing layer beyond the drawing and the flesh-color, then he refines the wrinkles and the eye socket with the flesh-color. After that he adds a uhitish tone to the flesh-color and applies it to the protruding parts of the face and finishes them with the highlight colors. Then he applies the reddish color, scumbles the shaded parts and outlines the contours, emphasizes deep wrinkles in old faces by the bolus and touches the upper eyelid with the fusing color.

It is evident that Hermeneia presents a genuine medieval method - a strictly ordered and gradual system of painting based on the following principle: previously made colors are built up layer onto a single overall ground layer.

Such a complete and harmonious system of face-painting as described by Hermeneia cannot be found very often, although its components can be detected in middle- and late-Byzantine painting. The Deesis icons by Theophanus the Greek is a lucky coincidence of the techniques used in practive and specified by instructions.

The face-painting in Theophanus' icons, as is also the case in Hermeneia, is a complicated system; it is actually a combination of the base layer, fusing layer, flesh-color, reddish bloom, lighter flesh color prepared from the whitish flesh color, and shading. The Greek painter used this method with amazing diversity, varying his accents from face to face in his icons. Specific modifications were dictated by the image he depicted.

The thing that was really important for Theophanus was color differentiation of the layers which obeyed the laws of shape variation in space. For instance, in Our Lady's face we can distinguish, under the dense white-highlight strokes, the following layers (from top to bottom): a lighter flesh-color, darker flesh color, ocher-pink fusing layer, and green ground color. If we move our gaze a little bit lower - to the center of the cheek - we can see that the thinner flesh-color layer is covered by the reddish tone; still lower, in the lower part of the cheek the reddish tone is on the fusing layer, and at the edge the base layer is covered with the brown shade. This sequence can be discerned in the above six icons with different modifications due to the various degree of face illumination. In the icon of Vasily the Great, that was traditionally attributed to Theophanus, the dense highlight strokes are applied directly to the fusing layer and the layer borders at the edge of the cheek are not shaded by the brown color. That is why I velieve that the face was painted by one of the artist's assistants.

The faces in the icons by the Greek master are painted with great thoroughness. The green overall base tone can hardly be seen as such but is visible through transparent colored scumbling layers. In the area of deep shades it is toned - sometimes, as in the Savior, by the fusing color and always by the brown glaze or layer. This shade is usually applied at the site where two colors - ground color and fusing or ground color and reddish color - meet. It creates an illusionary space where two color zones are mixed and whose boundary it smears. Therefore, the contour of the icons becomes sort of natural condensation of the shade; it also seems to be threedimensional in contrast to the more sharp and graphic lines in the face of Vasily the Great. The denser contrours can be seen in the faces of John the Baptist and Archangel Gabriel where they are accentuated by denser pigment layers. It is interesting that in Gabriel's face the density of shadows and brightness of contours are produced by the large content of the white lead of the flesh-color as well as by the daring and risky application of pure vermilion in the reddish bloom. The latter is applied as a very thin layer through which the flesh color can be discerned, which brings about the illusionary blending of the two colors. They are required by Hermeneia to be used in the reddish color and Theophanus adheres to this requirement. But of course we cannot find in any of Theophanus' icons such densely applied pigments as in Vasily the Great. The fusing layer is applied densely on the protruding parts and slightly reduced at the edges. Above it there are den-

se and hardly differentiated highlights without an interlayer. I believe that in the face of Vasily the Great we can distinguish the "shorthand" style which Hermeneia permits in murals. It can be assumed that the characteristics features of Vasily's figure were depicted by Theophanus' assistants: the colors, rather thick, were prepared in haste, the procedure used was not typical of the great master.

As a rule, the painting of master's icons is transparent, the layers are both very thin and very colorful. When preparing colors for the faces, Theophanus followed the recomendations of Hermeneia but enriched them greatly, employing minerals of unusually pure and concentrated colors: dark-blue lazurite, vermilion with a peculiar garnet tint, bright yolk-like ocher, and blackish-green glauconite. The Greek master used various types of blending; in this weg he enlarged the potential of medieval art with its indisputable rule - to prepare the colors in advance and not to mix them on the surface of the picture. We can discriminate three methods of blonding Theophanus used. One method is a conventional physical procedure: in order to obtain a specific color the necessary pigments are mixed with the binding media. In all likelikood, the experienced master took great care of the media because when he used lazurite he had to be very careful not to modify its color with an overconcentrated yolk. The master used both finely-ground pigments and coarse crystals and conglomerates that made the basis of the color spectrum of his colors. The second method was an optical or, as it is called in color science, three-dimensional blending of colors. This method can be successfully employed due to the outstanding virtuosity of the Greek master. The colorful layers applied one upon the other seem to merge giving rise to an illusion of being blended, to an imperceptible transition of one color into another. The main difficulty here is to know how to apply pigments in thin layers, using small brushes. Small ocher-pink strokes of the fusing layer mould the surface, following all changes in the volumetric form, and between the strokes the green color of the base layer is seen which produces the blending effect. The third method can be termed illusionary. Its principle is as follows. When coarse crystellites of the pigment are used which occur in the bottom layer of the overall ground tone the color of the upper layers (fusing, flesh-color, and whitish highlights) seem to roll down from their sharp edges without covering them. Therefore it appears that large intensively stained crystals of glauconite and lazurite occur in the upper pinky layers as an admixture which is not true. Due to this, the external light being refracted at their sharp edges produces a color play and enlivens the coloring.

One of the final modelling stages is the application of the white highlights. Normally, investigators indicate that the Greek master uses them with great temperement and impulsiveness. As a matter of fact, they obey a specific system. When analyzing the system, we can understand how serious and rigorous Hermeneia's instructions are. Their aim is to make very organic the relation between the previous stages of modelling with the white-color finish. Hermeneia recommended to add the white lead to all dependent colors in order that the shape can endure the load of the dense paint. Theophanus excellently used white lead in the fusing layer and in the flesh color, transforming them into a plastic and flexible mass that can be converted into a colorfully-molded shape.

The basic feature of Theophanus' system is the conjugation of white-paint strokes. Most frequently it is a combination of two or several parallel strokes that are repeated many times and have a rounded shape. One of the strokes is powerful and dense; this is the major one; adjacent to it there are thin strokes that act the part of the supporting voice. This row of minor strokes facilitates the spatial propagation of the light of the major one, characterizing the shape in its great complexity and diversity. This system of lights is very constructive and informative. It is in agreement with the requirements of the composition and iconography: no matter whether it is a face painted en face or in three quarters, whether it is a young or an old face. When the Greek master employs dense white highlights, as in the face of Our Lady or John the Crysostom, applying a large number of the whitish flesh color under the pigment. But he painted many faces with a very moderate amount of white in highlights, e.g. the Savior, John the Baptist Archangel Gabriel. Here we can see that the strokes are thin and long, while in the faces of Apostle Paul and John the Chrysostom they are thick, rounded, and compact. The most complicated shape of highlights of the suborbital cavity can be seen in the three-quarter faces of Our

Lady and John the Chrysostom. In the face of Vacily the Great the strokes are poorly executed: the thick stroke is divided into very few minor strokes.

It is beyond doubt that the face of Vasily the Great is made by a Theophanus' assistant. His individual manner was not to find his own approach but to adapt the mural skills to convey the image of the saint, full of energy, passion and great will, as Theophanus thought him to be. It appears that this assistant could not maintain the essense of the image during his long-term and strenuous work. His inspiration was sufficient for "shorthand" painting.

In conclusion, analysis of the techniques used in the XIVth century art, which was the most sophisticated in Byzantine painting, can be improved if we make use of the Hermeneia text that canonized the methods of Paleologus painting.

Working Group 24

Rock Art

Art rupestre

EMBRES

. Brunet (France)
. Vidal (France)
. Vouvé (France)
. Waingright (Canada)
. Haschid (Algérie)
. Tellechea (Argentine)
. Rosenfeld (Australie)

GROUPE DE TRAVAIL ART RUPESTRE

Coordinateur
Eduardo Porta
(Espagne)

PROGRAMME 1987 - 1990

1. Etablir un système de communication entre les membres du groupe de travail afin d'échanger les informations relatives aux thèmes de la conservation de l'art rupestre. On envisage la publication d'un bulletin.

2. Procurer la liaison avec les autres groupes qui peuvent avoir des problèmes semblables et qui ont déjà développé des systèmes de restauration compatibles avec ceux de l'art rupestre, principalement les groupes de peinture murale et le groupe de la pierre.

3. Développement de nouvelles méthodes de nettoyage des graffitis et inscriptions qui ont été ajoutés aux lieux préhistoriques.

4. Etudier les problèmes des adhésifs vis à vis de la conservation en plein air et dans des endroits soumis à l'action des eaux, du soleil, du changement thermique.

5. Préparer des programmes de formation spécifiques pour les gens qui s'interessent à l'art rupestre, encourageant les institutions nationales et internationales à promouvoir des réunions de spécialistes à tous les niveaux, et appuyer les programmes de formation.

RESUME

L'analyse en laboratoire de prélèvements faits sur les parois des abris peints du plateau du Tadjilahine du TASSILI N'AJJER, a permis l'étude de la stratigraphie picturale des peintures et de connaître mieux leur composition chimique de même que la nature des produits d'altération.

Fig 1 : Localisation du TASSILI N'AJJER

ANALYSES DE PRELEVEMENTS DES PEINTURES DES ABRIS PEINTS DU PLATEAU DU TADJILAHINE (TASSILI N'AJJER) - ALGERIE

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Introduction

Situé à près de 1500 Km de la Méditerranée, le Tassili N'Ajjer est un vaste plateau de la partie orientale du Sahara central (Fig 1). Sur ces étendues désertiques bordées au sud et au sud-ouest par des abrupts hauts de 500 à 600 m, d'importants massifs rocheux sont dispersés. Ceux-ci ont été modelés au cours des temps géologiques durant lesquels l'action des intempéries a creusé, élargi, taraudé les fissures, les fractures, tous les accidents de cette masse gréseuse pour donner naissance aux paysages tels que nous les connaissons : gorges profondes, colonnes de pierres, impressionnants surplombs rocheux, chaos...

Les auvents, les abris au bas de ces blocs, les parois rocheuses ont pu servir de lieux de campement et/ou être le support de manifestations artistiques (peintures-gravures). Depuis le Néolithique, le climat a évolué puis est devenu d'une sécheresse extrême à part quelques précipitations rares et sporadiques. De multiples paramètres expliquent le maintien en bon état ou la dégradation de ce patrimoine archéologique ; un bilan s'imposait donc.

Dans ce sens, la République Démocratique et Populaire Algérienne mène des actions concertées avec différents services et le concours de l'UNESCO et de l'ICOMOS, afin de mieux assurer la conservation de cet art rupestre de plein air. Dans ce contexte, nous avons été conduits à faire l'inventaire des problèmes de conservation et depuis 1979, en collaboration avec l'Office du Parc National du Tassili, une prospection systématique des sites est entreprise pour recenser les phénomènes susceptibles d'affecter la conservation des oeuvres rupestres.

Rappelons ici que la conservation est un travail d'équipe à la convergence de différentes disciplines et dans ce cadre il convient d'apporter un diagnostic scientifique portant sur la connaissance des peintures et des altérations qui les affectent.

En septembre 1985 au cours d'une mission sous les auspices de l'ICOMOS et de l'Office du Parc National du Tassili, nous avons pu étudier ces questions au niveau des abris décorés du plateau du Tadjilahine sur les sites d'Essalam Ouan Amis, d'Iheren et T-i-n Abanhiar à environ 250 km au nord-ouest de Djanet (Fig 2 - ci-dessous).

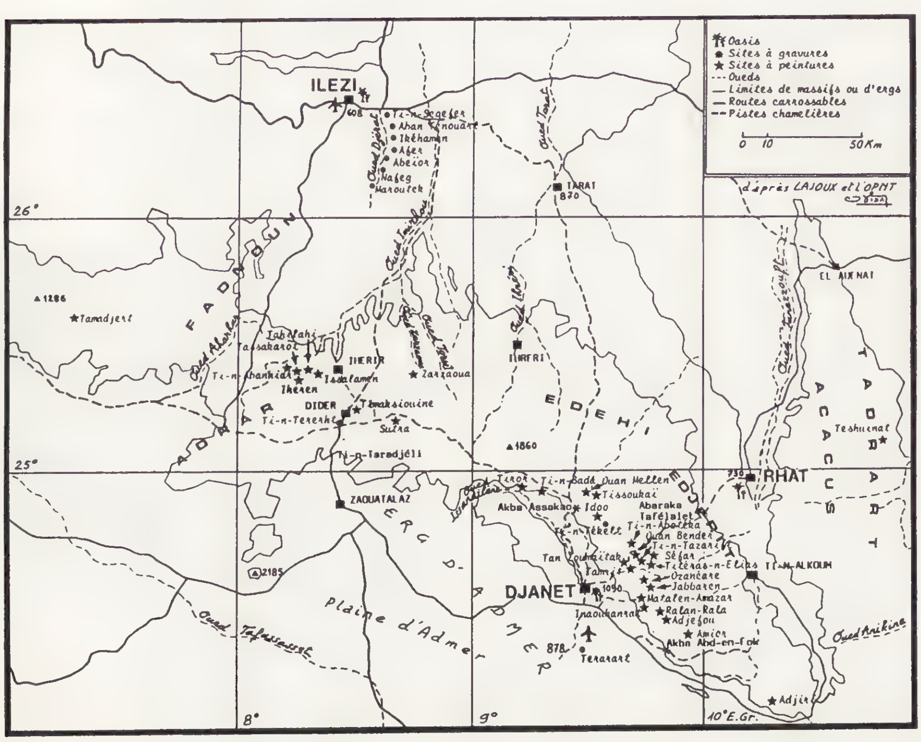

Fig 3 : Situation des abris d'IHEREN

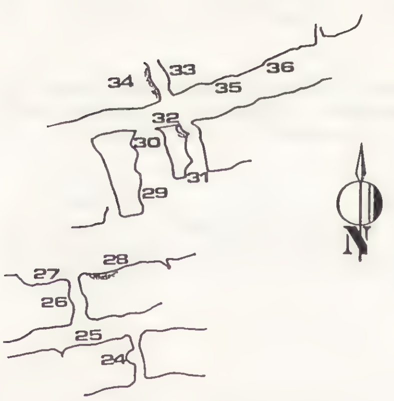

Fig 4 : Situation des abris de T-i-n Abanhiar

1) Stratigraphie picturale des prélèvements

16 échantillons ont fait l'objet d'une étude à partir de sections polies, observées sous la loupe binoculaire et de tests de microchimie. Nous ne mentionnerons que les prélèvements les plus représentatifs des abris d'Iheren, Essalam Ouan Amis et T-i-n Abanhiar.

. I.H. 14 : prélèvement de couleur rouge vif, réalisé sur une ponctuation de l'abri n°1 de Iheren (Fig 3).

L'examen révèle une superposition de 3 couches (Photo 1) :

- une couche blanchâtre de quartz où l'analyse décèle du carbonate de calcium et des sulfates (couche n°1)
- une couche orange d'ocre rouge avec du fer (couche n°2)
- une couche brunâtre mêlée de petits grains de sable (couche n°3).

. I.H. 15 : prélèvement sur le bord de la figure rectangulaire, de couleur rouge vif de l'abri n°1 d'Iheren. Un petit accident de la paroi a été mis à profit pour le prélèvement.

Nous observons (Photo 2) :

- une couche blanchâtre de grains de quartz avec présence de carbonate de calcium et de sulfates (couche n°1)
- une couche orange d'ocre rouge (avec du fer) (couche n°2).

. T.A.B. 20 : prélèvement réalisé dans l'abri n°34 de T-i-n Abanhiar (Fig 4) sur un personnage aux contours de couleur rouge. Le support est en mauvais état et les tracés sont sur une formation en cours de décollement et présentant des boursouflures.

L'observation révèle (Photo 3) :

- une couche blanchâtre de quartz avec présence de carbonate et de sulfate (couche n°1)
- une couche fine orange constituée d'ocre rouge (couche n°2) (Fig 4)

. T.A.B. 23 : prélèvement dans l'abri n°34 de T-i-n Abanhiar au niveau des pattes antérieures d'un bovin rouge et blanc.

L'étude optique décèle 3 couches (Photo 4) :

- une couche blanchâtre avec des gros cristaux de quartz, où l'analyse révèle la présence de carbonate et de sulfate de calcium
- une couche blanche composée de sulfate de calcium
- une couche rouge d'ocre.

. T.A.B. 24 : abri n°34. Prélèvement au niveau du bovidé jaune aux cornes en forme de lyre ; effectué en bordure d'une lacune due à la chute du support décoré.

L'étude montre (Photo 5) :

- une couche blanchâtre avec des cristaux de quartz ; elle contient des carbonates et des sulfates (couche n°1)
- une couche jaune d'ocre jaune (couche n°2).

. T.A.B. 29 : abri n°32 de T-i-n Abanhiar. Prélèvement de peinture blanche sur une figuration bicolore ; le support est soulevé.

L'étude stratigraphique indique (Photo 6) :

- une couche avec de gros cristaux de quartz blanchâtre avec présence de sulfate et de carbonate (couche n°1)
- une couche blanche de sulfate de calcium (couche n°2)
- un mince liseré marron de poussières de quartz.

Les études stratigraphiques de ces prélèvements permettent de différencier des modèles à deux couches et à trois couches. La couche n°1 a été arrachée lors du prélèvement au support - le grès - et ce n'est pas étonnant d'y trouver les grains de quartz accolés les uns aux autres ou cimentés. La présence de carbonate et de sulfate peut s'expliquer soit par leur existence naturelle dans le grès qui est un dépôt fluviatile ou par migration et concentration par l'eau circulant entre les grains. La couche n°2 quand elle est rouge ou jaune contient de l'ocre (rouge ou jaune selon les cas) ; quand elle est d'autres couleurs nos déterminations sont plus délicates et révèlent le sulfate de calcium quand il s'agit de blanc - c'est le cas de T.A.B. 29.

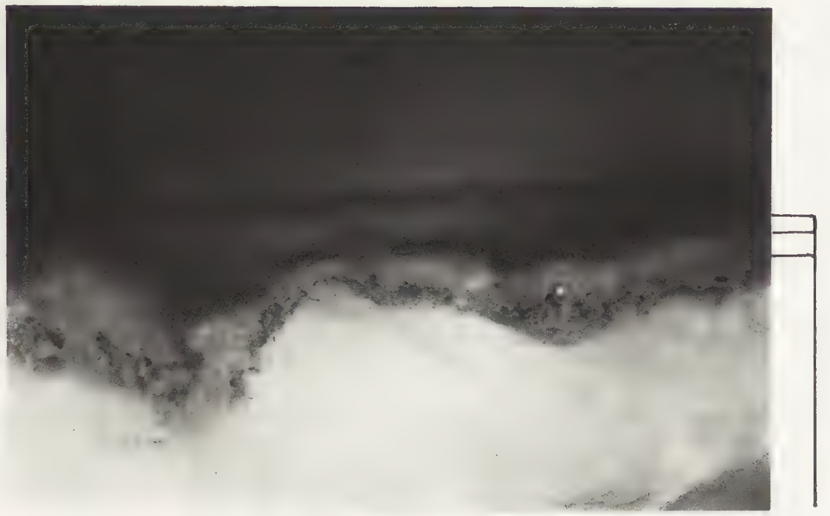

Photo 1 : Coupe stratigraphique de I.H.14 :
1. Coupe blanchâtre (carbonate, quartz, sulfate)
2. Couche orange (ocre rouge)
3. Couche brunâtre (sable)

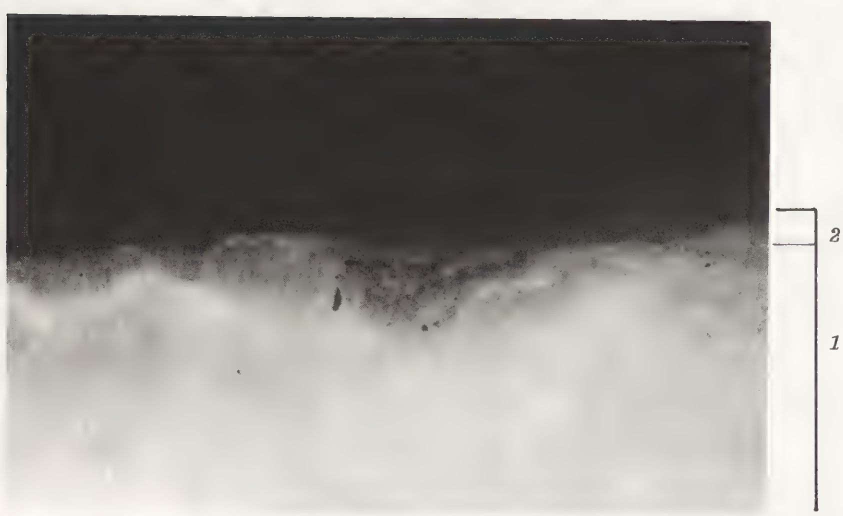

Photo 2 : Coupe stratigraphique de I.H.15 :
1. Couche blanchâtre (carbonate, quartz, sulfate)
2. Couche orange

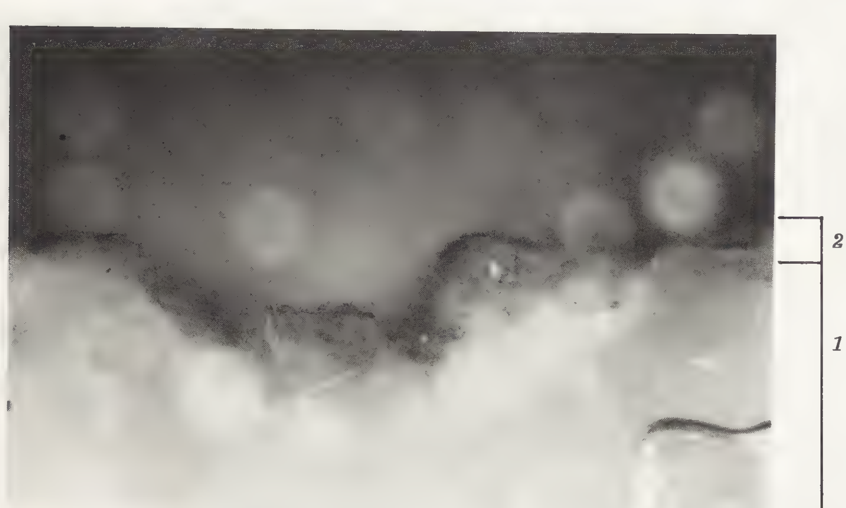

Photo 3 : Coupe stratigraphique de T.A.B.20 :
1. Couche blanchâtre (carbonate, quartz, sulfate)
2. Couche fine orange (ocre rouge)

Photo 4 : Coupe stratigraphique de T.A.B.23 :
1. *Couche blanchâtre (carbonate, quartz, sulfate)*
2. *Couche blanche (sulfate de calcium)*
3. *Couche rouge (ocre rouge)*

Photo 5 : Coupe stratigraphique de T.A.B.24 :
1. *Couche blanchâtre (carbonate, quartz, sulfate)*
2. *Couche jaune (ocre jaune)*

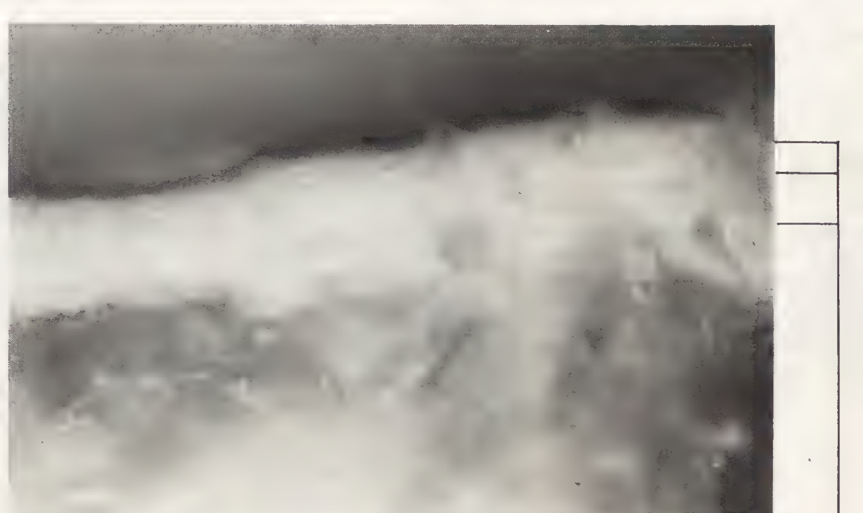

Photo 6 : Coupe stratigraphique de T.A.B.29 :
1. *Couche blanchâtre (carbonate, quartz, sulfate)*
2. *Couche blanche (sulfate)*
3. *Liseré brun de poussière de quartz*

2) Résultats des études par spectrophotométrie infrarouge

Ces études ont porté sur les peintures et sur les produits d'altération (efflorescences - poussières) les recouvrant.

. 2.1 Dépôt en surface des peintures

- T.L. 7 : poudre et efflorescences blanchâtres d'un abri d'Essalam Ouan Amis - mise en évidence de sulfate.

- I.H. 8 : croûte de couleur jaune présentant des boursouflures, pouvant recouvrir les peintures ; issue de l'abri niche n°7 d'Iheren. Riche en sulfate de calcium.

- T.A.B. 19 : prélèvement réalisé dans l'abri n°34 de T-i-n Abanhiar au niveau d'une croûte en voie de détachement de la roche. Présence de sulfates et silicates. Ces formations en croûtes soulevées de la paroi sont donc riches en sulfate de calcium ; elles correspondent à toute une évolution déjà décrite par les spécialistes de la "maladie de la pierre".

. 2.2 Au niveau des peintures

La recherche de liant après le processus classique d'extraction par le chloroforme s'est révélée négative. Les peintures contiennent aussi des sulfates ; pour les peintures rouges ou jaunes, les sulfates issus de produits d'altération de la roche ont pu migrer.

3) Résultats avec utilisation de microscope électronique à balayage et sonde électronique

Des résultats complémentaires ont été obtenus au microscope électonique à balayage et à la sonde électronique à l'Institut Textile de France par observation de prélèvements et de sections polies, préalablement métallisés avec de l'or.

. T.A.B. 24 : le prélèvement, rappelons-le, vient d'un bovidé jaune de T-i-n Abanhiar ; l'analyse de la surface ornée révèle de manière qualitative la présence de fer, de calcium (en fortes proportions), de trace de sodium, de soufre.
Le balayage par un faisceau d'électrons du même échantillon, en section polie met en évidence dans la couche externe (pigments), la présence de fer, calcium, potassium et soufre (Fe, Ca, K, S).

. T.A.B. 28 : prélèvement sur un bovidé de couleur verte de T-i-n Abanhiar. Examen de surface : détection de Fe, Ca et K, beaucoup de silicium (c'est normal la roche est un grès) et du soufre. Examen en section polie : S, Si, K et Ca.

. T.A.B. 22 : prélèvement sur une peinture de bovidé blanc de T-i-n Abanhiar. Examen de surface : Si, Ca, S, absence de K, détection de titane. Examen de section polie : la couche déterminée comme couche pigmentaire par examen stratigraphique renferme du Ca, du S, des traces de K, le titane a disparu et absence de silicium. Pour cet échantillon T.A.B.22, l'absence de Si au niveau de la couche pigmentaire et la présence de Ca et S paraissent éliminer l'hypothèse d'un pigment blanc à base d'argile dont le réseau cristallographique contient en principe abondamment du silicium. Ce pigment blanc serait donc un sulfate : gypse ou anhydrite, qui sont les plus courants.

. I.H. 15 : prélèvement sur une figure rectangulaire rouge. Examen de la section polie : présence de Ca, S, Fe, Si. Le fer n'est pas réparti de manière homogène, mais est concentré en micronodules. Ces concentrations apparaissent déjà lors de l'examen des sections polies.

. T.A.B. 25 : prélèvement sur un bovidé de couleur rose pâle. L'examen de la section polie en microsonde révèle la présence de calcium et de soufre dans la couche superficielle, avec peu de silicium et un peu de fer. La couleur rose observée à l'oeil nu sur le terrain serait alors due à une faible concentration d'ocre rouge. C'est une hypothèse.

. T.A.B. 20 : l'étude des rayonnements émis après balayage de la section polie par un faisceau d'électrons a décelé la présence de fer, calcium et titane. Cette microsonde permet d'obtenir la répartition cartographique de certains éléments chimiques et nous avons pu mener cette étude sur une petite dépression en bordure de la section polie. Nous avons pu examiner cette petite zone, sans changer ni le grossissement (x 240) ni l'orientation, pour mieux connaître la répartition du silicium, du calcium, fer et titane (sur les clichés polaroïd obtenus les points clairs sont des zones de forte densité de l'élément excité et inversement les zones sombres et noires de faible densité ; un faible fond continu persiste cependant) :

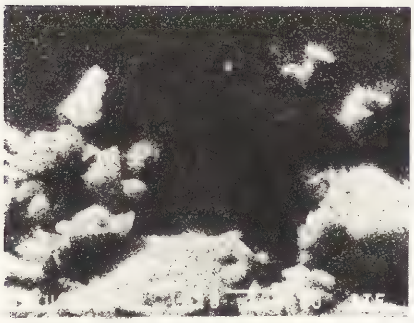

Photo 7 : Localisation du silicium dans l'échantillon T.A.B.20

Photo 8 : Localisation du calcium (même échantillon)

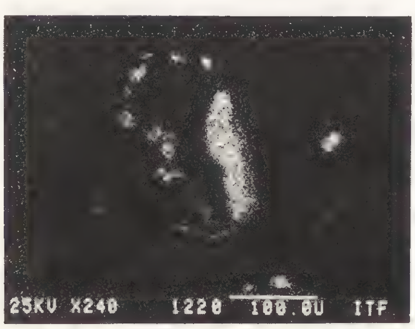

Photo 9 : Localisation du titane (même échantillon)

Photo 10 : Localisation du fer (même échantillon)

- Photo 7 : l'excitation du silicium souligne la localisation des grains de quartz
- Photo 8 : les zones claires correspondent à la localisation du calcium, uniquement dans la petite dépression
- Photo 9 : localisation du titane dans la partie centrale de la petite dépression sous forme d'un granule longiligne et sous forme de petites taches en bordure de cette dépression
- Photo 10 : localisation du fer, en partie associé au titane au fond de la dépression.

Sur un exemple précis choisi, ont été observées des cartes de répartition d'éléments chimiques (Si, fe, Ca et Ti) ; ces documents permettent de mieux cerner la dépendance ou l'indépendance des éléments étudiés. Ainsi la répartition du Fe et Ti est indépendante du Si ; par contre Fe et Ti sont en partie associés. Cette méthode malheureusement onéreuse ne doit pas se substituer aux analyses traditionnelles et, disons-le, les plus "banales", mais au contraire venir pour renforcer un diagnostic, c'est dans ce sens où nous l'avons employée.

4) Analyse qualitative par fluorescence X

Les échantillons non broyés, en raison du peu de matière dont nous disposions et de l'impossibilité de séparer les pigments de la roche, ont fait l'objet d'une analyse qualitative. Pour les échantillons de couleur rouge et jaune, l'analyse révèle la présence de silicium, calcium, soufre, potassium, titane et confirme ce que nous savions par d'autres méthodes ; pour les prélèvements blancs, notons la présence de soufre et de calcium et absence d'aluminium qui aurait pu nous orienter vers des pigments à base d'argile. Pour ce dernier point, d'autres analyses complémentaires sur de nouveaux échantillons seront nécessaires.

Conclusions

Les peintures analysées ont une stratigraphie picturale simple, la paroi ne paraît avoir subi aucun traitement préalable. Les pigments utilisés sont d'origine minérale et ce sont des ocres (rouges et jaunes) et seraient des sulfates pour le blanc.

Depuis le Néolithique, un léger dépôt à base de sulfate s'est formé sur les parois ; dans le contexte climatique actuel - très aride - cela paraît favorable à la conservation des peintures.

Remerciements

Il nous est agréable de remercier, la section des Pays Arabes de la Division du Patrimoine Culturel de l'UNESCO, les services de l'ICOMOS, les services de l'Office du Parc National du Tassili, Messieurs BOZELLEC, CALLEDE, COLOMBINI et Madame TUDELA du L.R.M.H.

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SUMMARY

It is believed that the primary weathering processes on the art at Walga Rock, involves the presence of water. A model based on micrometeorological studies by Lyons[1] has been applied to consider what incidence of condensation there may be on the art. The other source of water damage is recognised as being due to driving rain.

The model is primarily based on the surface energy balance, where each point on the rock face, its heating and cooling trends, are directly related to their respective sky view-factors. The sky view-factor is the real proportion of surface directly exposed to the sky. This model was used to predict rock face temperatures, and in conjunction with climatological data from nearby Cue, was then used to study the incidence of dew-point temperature on the rock face.

The model did not predict condensation on the rock face via the processes of dew formation or fog inception, for either current site conditions or conditions of revegetation. However, the moisture input from vegetation transpiration into the microclimate is recognised in that it would have some effect on the kaolinitic pigments, the extent of which has not yet been ascertained.

Taking into account the action of driving rain and transpiration, a management proposal has been drawn up. This proposal seeks to minimise rain action, combined with a cautious approach to the questions of humidity and condensation.

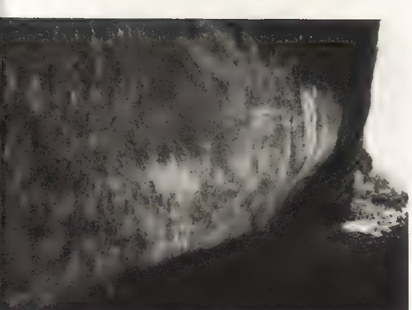

Fig. 1: Walga Rock shelter, near Cue, Murchison District, Western Australia.

THE USE OF MICROMETEOROLOGICAL STUDIES AS AN AID TO THE CONSERVATION OF ABORIGINAL ROCK ART

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Introduction

In recent years the need for conservation of aboriginal paintings has become increasingly recognised. There has been a growing awareness of the important and integral part that rock art plays in Australia's heritage.

Conservation processes are generally individually considered to take into account the specific characteristics of each site. For example, sites located in more arid conditions are generally more stable with regard to aboriginal rock art, and less conservation work is necessary. However, with sites where more marginal climatic conditions prevail, the patterns and processes of weathering must be understood so that the most effective management programmes may be implemented. Whilst weathering is a natural and inevitable process, factors within a micro-environment may either enhance conservation, or hasten deterioration. The application of these programmes must also demonstrate the appropriate respect and sensitivity toward maintaining the natural integrity of the site.

Walga Rock art site suffers weathering processes that have not yet been clearly understood. This paper aims to pinpoint the major variables within the weathering processes, and discuss the relative importance of each of these.

This study aims to identify both the past and present weathering processes, and also future processes that may occur in the advent of an implemented management plan, which would consider the variables that have been discovered during the course of this research.

There are three major data sources incorporated within this study programme and they include the use of climatological data recorded at Cue by the Bureau of Meteorology, field data recorded within the art site itself and the implementation of a micrometeorological model, developed by Lyons[1], which is based upon predictions of the heating and cooling trends on the rock face.

The field data assists in testing the validity of the model, which can then be used in conjunction with the climatological data to predict the temperature trends on the rock face.

Methodology

It has been recognised that the deterioration of the art at Walga Rock is hastened by water[2]. White pigments, being kaolinitic clays, are particularly sensitive to water. The three situations that will lead to hastening of the weathering processes are: (i) water reaching the rock face by means of driving rain; (ii) the condensation of water on the rock face, when the dew-point temperature has been reached; and (iii) the condensation of water on the rock face via the mechanism of fog inception.

The aim of this paper is to study the micro-environment within the rock shelter to see if it is at all possible that water might condense on the rock face. The effects of change in this micro-environment, brought about by different variables such as vegetation height and transpiration will also be examined.

Finally, a management plan is described so that the site conditions can be enhanced to provide a greater control over the weathering variables.

Site Description

Walga Rock is situated 45km west of Cue in the upper Murchison Region of Western Australia. Of the 60m long wall which carries an extensive array of rock paintings, this work has been concerned with those paintings within the shelter (see Figure 1). The shelter's dimensions are: 25 metres long, 12 metres high and up to 5 metres deep at the widest point. The paintings within the shelter extend the full length of the shelter, and up to a height of 2.5m. Carbon dating of deposits within the floor of the shelter denote human occupation back to 9950±750 years B.P.[3]

Predominantly there are two pigments used in the paintings, as have been identified by Clarke[2] - the red pigment, hematite (Fe_2O_3) and the white pigment, kaolinite ($Al_2Si_2O_5(OH)_4$). The white kaolinitic clay pigments display much more deterioration than those based on hematite. The reason for this is that the kaolinitic clay is much more susceptible to moisture and changing humidities, due to the hydration of the molecules which causes dimensional changes which can lead to the pigment being dislodged from the rock face. Hematite, on the other hand, is unaffected by the presence of

moisture, and bonds very strongly to the rock face.

The two forms of moisture which present problems are firstly, water in the liquid phase and secondly, humidity changes. The effects of humidity on stability are far less dramatic than the presence of water itself. Since the magnitude of the effects of humidity changes on weathering are markedly less than those associated with water in the liquid phase, we have concerned ourselves primarily with the latter.

There are four ways by which water may reach the rock face and contribute to the weathering of the paintings. The four modes are: water seepage through the rock face via fissures; rain being driven onto the rock face; the condensation of water on the rock face in the form of dew; and the condensation of water on the rock face through fog inception. Each mode of weathering is assessed below.

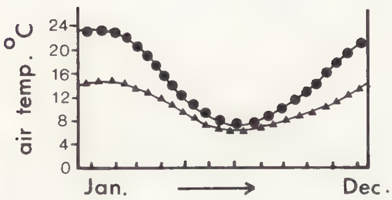

Fig. 2: Minima and dew-point temperatures for Cue. Data courtesy of the Bureau of Meteorology. Dew-points▲ Minima ●

Water Seepage

The action of water seepage on the rock face is localised and damage minimal. Since Walga Rock is granite and has a negligible porosity, water seepage is only through fissures. The effects of the water seepage occur only at the weathered edge of the shelter, with drainage occurring only after rains.

It is not considered necessary to divert this streaming since the diversion would only transfer the problem and the damage to a more sensitive part of the site.

Driving Rain

A study to determine the incidence of driving rain in this area needs to be done to fully evaluate this problem. It is calculated that rain would have to be driven at an angle of 27° to the vertical, to place water on the rock face at a height of 2m or lower. It is understood from Pigdon[4] that in the 1930's the site was well sheltered by vegetation, and it is since that period that the site has been largely cleared. The clearing process has probably increased the incidence of rain-based weathering. Support for this argument was found during field work when a light rain shower resulted in small amounts of water being driven onto the wall.

Management of this problem may be best served by replanting the area with the original and indigenous species since this would serve to both shelter the site from possible rain, and restore the former integrity of the site. However, vegetation transpiration may then result in the condensation of water on the rock face. This problem is addressed in a subsequent part of the text.

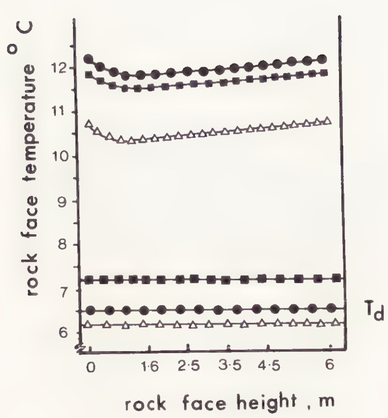

Fig. 3: Predicted minimum temperatures : a vertical temperature profile of the rock face for the months June■, July△ and August ●, with their corresponding dew-point temperatures.

Water Condensation

It is the consideration of water condensation through the mechanisms of dew formation and fog inception that forms the basis of this research programme. We are concerned with both an assessment of current conditions and a projection of future parameters with vegetation regrowth, in our attempt to model the incidence of these forms of condensation.

Modelling

Lyons[1] has developed a computer model based on the surface energy balance, where predictions can be made of the heating and cooling rates of various surfaces: in this case the rock face. Predictions for Walga Rock are made to cover the whole diurnal range for each month of the year. This was done by modifying the model to suit site conditions[5].

The method of collating a year's predicted data initially involved recording in the field. Rock face temperatures were taken over several days, and then one of these diurnal ranges was extracted and compared with predicted data from an initial model run. This enabled the model to be finely tuned, to produce a close match of actual and predicted data, leading to extrapolation of data for each month of the year.

The criteria under which the days' field data was selected to compare with the model's data, were conditions of optimal cooling, where relatively lower minimum rock face temperatures were reached: through clear skies and minimal wind conditions.

A further explanation of the field data collection and the mathematical bases of the model, are contained in the full report[5].

Once the model had been developed to an acceptable level, the predicted data could be compared with long-term Bureau statistics for the Meteorological Station at Cue, to ascertain the likelihood of condensation occurring on the rock face through dew-fall.

Average Conditions Over 12 Months

The temperature at which dew forms from moisture in the air is called the dew-point. Analysing the Bureau's data for Cue, Figure 2 demonstrates the times

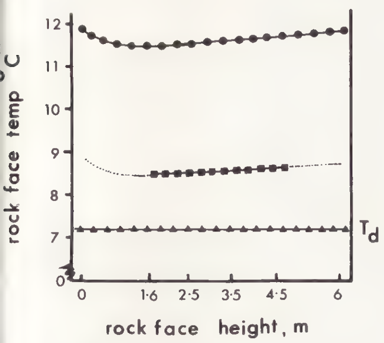

Fig. 4: Predicted rock face minimum temperatures ······ under extreme conditions ■ recorded at Cue on 7, 8, 9 June 1983. The predicted vertical rock face temperature profile under extreme conditions, is lower than normal ●, but still well above the dew-point▲.

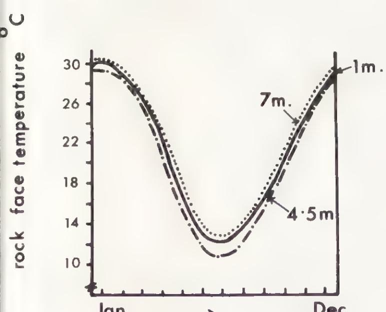

Fig. 5: Predicted data : monthly rock face minimum temperatures, at rock face height of 0.0m, for vegetation heights of 1.0, 4.5 and 7.0 metres.

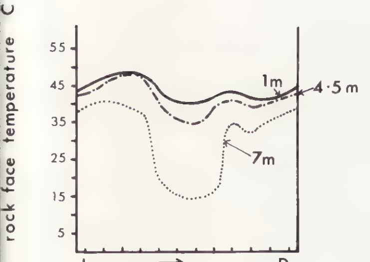

Fig. 6: Maximum rock face temperatures at 1.6m on the rock face for vegetation heights of 1.0, 4.5 and 7.0 metres.

of the year where the minimum air temperature and the dew-point temperature are in close proximity to each other. The months of June, July and August are the most susceptible for dew-fall to occur. It must be rememberd that this comparison is for air temperature minima, and not rock face temperature minima. The mechanism for dew-fall is such that if a surface temperature drops to the dew-point temperature of the surrounding air, then dew will condense on that surface.

Figure 3 demonstrates the predicted minimum rock face temperatures for June, July and August, and the proximity to their relative dew-point temperatures. The data in Figure 3 clearly demonstrates that under average conditions dew will not form on the rock face, which leads to an investigation into extreme temperature conditions to see if they can give rise to water condensation.

Rock Face Minima - Extreme Conditions

Some extreme daily minimum air temperatures were recorded at nearby Cue in 1983, on June 7, 8 and 9, with respective temperatures of 3°, 1° and 4°C. The model was altered to run a series of predictions for these conditions. Figure 4 shows the predicted rock face minimum temperatures for June for both the normal conditions and under the extreme conditions. The data indicates that dew-point may not be reached even under the extreme cold temperatures noted above.

On the assumption that the mathematical model is valid, it has been shown that dew will not condense on the rock face under normal or extreme conditions, under the current site situation. The effect of vegetation must now be examined, since it has a major influence on rock face temperature and dew-point involving both sheltering capacity and the vegetation transpiration.

The Effects of Vegetation Heights on Rock Face Temperatures

If the area in front of the cave is revegetated, there are two outcomes influencing the rock face temperatures. Firstly, the heating of the rock face, currently assisted by direct sunlight, would be lessened due to shading, and as a body's cooling rate is proportional to its magnitude in temperature, the cooling rate would be lowered. Secondly, the night-time long wave emission by the rock face, which lowers the rock face temperature, would be partially blocked by the vegetation, and hence this too would lessen the cooling rate.

The overall outcome is to lower the diurnal temperature range - thus cooler rock face maxima and warmer rock face minima are experienced. Figure 5 represents the rock face minimum temperature at ground level at vegetation heights of 1.0m (current), 4.5m and 7.0m. The temperature differences for each vegetation height are not as great for higher points on the rock face. Figure 6 shows rock face maxima at 1.6m height on the rock face for differing vegetation heights. Comparison of the data for the two heights of rock face shows that the vegetation has a minimal effect on rock temperatures at ground level but has a major effect at the 1.6m level.

Transpiration from Differing Vegetation Heights

Condensation may be formed on the rock face by dew formation and by fog inception. Both phenemena will affect the deterioration of the rock art and they are discussed below since they influence the implementation of the proposed revegetation programme.

Dew Formation

With no specific local data available on leaf area indices and transpiration rates of plants, representative figures were chosen using vegetation transpiration rates suggested by Attiwill and Clayton-Green[6],* and a suggested leaf-area index[7]. The transpiration rates can be calculated using their data and expressed as kg water $day^{-1}m^{-3}$ vegetation. The results show that $1m^2$ leaf-area yields 2.64kg water day^{-1}, and that $1m^2$ leaf-area is the equivalent of $5m^3$ vegetation. The above data was then used to assess whether transpiration could induce condensation through dew-fall.

To do this, parameter time periods were chosen to represent the air residence time and moisture build-up: ½ hr and 24 hrs. Without researching local conditions at length, it can only be said that the real value may lie somewhere in between these two parameters. Further assumptions made in the calculations were that there is a uniform mixing of air within the cave and that all the transpired moisture would maintain the appropriate air residence time within the shelter. It was also assumed that there is no mixing of air whatsoever across the boundary of the cave and the external environment within that air residence time. The results of the calculations for the amount of water required to achieve dew-point on the rock surface are shown for each month in

*Transpiration rate chosen from E. Microcarpa for moderate stress am/pm to 5.95mml kg^{-1}dry wt s^{-1}.

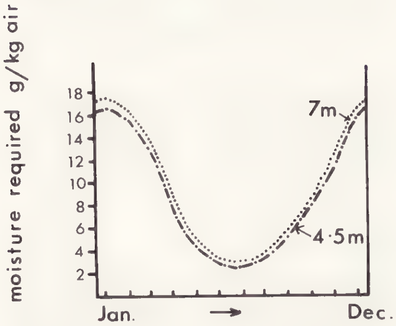

Fig. 7: The required gm H_2O/kg air for each month, if condensation is to be reached on the rock face by the dew-point rising and enveloping the minimum rock face temperature at 1.6m: for 4.5m and 7.0m heights of vegetation.

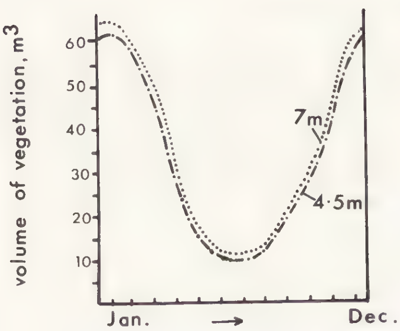

Fig. 8: The volume of vegetation required for an air residence time of 24 hours, transpiring at the given rates needed to raise the dew-point temperature to envelope the minimum rock face temperature at 1.6m: for vegetation heights of 4.5m and 7.0m.

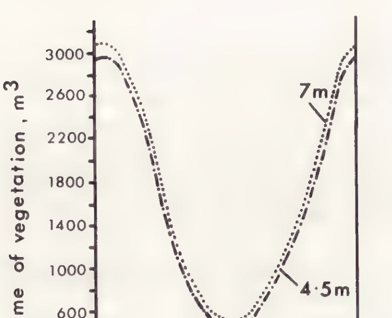

Fig. 9: The volume of vegetation required for an air residence time of ½ hour, transpiring at the given rates to cause the dew-point temperature to meet the rock face temperature at 1.6m: for vegetation heights of 4.5m and 7.0m.

Figure 7. The amount of vegetation required to achieve the mass of transpired water is shown in Figures 8 and 9 for the two extremes of air residence times of 24 hours and half an hour respectively.

The huge volume of vegetation required for a ½ hour air residence time shows the system to be unrealistic, which leads to the conclusion that dew would not form within these small air residence times as a result of planting trees and shrubs at Walga Rock.

The volume of vegetation required for a 24 hour air residence time may be quite realistic, but it is questionable as to whether dew could actually fall. Monteith's[8] studies indicate that windspeeds of over $0.5ms^{-1}$ at a 2m height are required to facilitate dew-fall, and these windspeeds are not conducive to the long air residence times within this shelter.

Fog Inception

Having 'removed' the problems of driving rain through vegetation cover and shown that condensation through dew-point formation, as a result of increased transpiration, is unlikely, the final point to consider is fog inception. A fog comprises condensed water droplets in the air, when dew-point is reached in the air. When this happens all surfaces within the area become saturated due to the fog's inception regardless of their temperature. This phenomenon was recorded on site on May 15, 1986. However, it was noted that the rock face was the only surface that wasn't saturated. Within several metres from the rock face, the fog thinned out, preventing water condensation on the rock face. This may be due to the thermal capacity of the rock, warming the ambient air, combined with the possibility that there is insufficient air movement in fog conditions, to assist in the placement of water on the rock face in this situation.

It may then be concluded that neither dew formation nor fog inception would present a major problem, due to the lack of mechanisms enhancing the placement of water on the rock face. It is recognised, however, that the question remains as to what degree the humidity of the air may affect the condition of the paintings. There is no control that may be exercised over the incidence of fog, nor its effects regarding humidity, though in relation to revegetation there may be controls that could assist in the dispersion of transpired moisture through greater volumes of air so as not to aggravate the problem. This is outlined in the management proposal.

It is felt that due to the great potential damage of rainfall, the best way of maintaining the site's integrity is through the planting of vegetation since any transpiration-related problems will be of a much smaller magnitude than driving rain.

Management Proposal

The management proposal revolves around a revegetation programme to be undertaken around the vicinity of the rock art wall. This is not only justified on scientific grounds, but it will also help to restore the integrity of the site.

The first proposal includes a revegetation programme that should be undertaken to offer the paintings, particularly in the shelter, some protection from driving rain. Large trees, indigenous to the site with a mature height of 7-8m should be planted marginally exterior to the drip line. An understorey of vegetation should be arranged so as to suit the second type of protection plan. The placement of the understorey vegetation should be arranged so that a side-profile of the vegetation should appear as though a solid wall (particularly to lower cooling rates of the rock surface) and the aerial view should demonstrate a staggered pattern to maximise the ventilation of the shelter as shown in Figure 10.

The lowering of the day-time heating rates and the night-time cooling rates is achieved by the reduction of the degree of direct sunlight on the wall, and a blockage of long-wave emissions from the rock face at night.

The ventilation is required to minimise the air residence times within the shelter and to guard against the build-up of humidity.

It is important that this revegetation should not take place in the immediate vicinity of the rock wall, as this may create a fire hazard. Clarke's studies[9] have shown the magnitude of rock surface heating from fires and as such, a fire could destroy most of the painted surface.

Conclusion

The weathering problem, demonstrated by the deterioration of the kaolinitic-clay based paint, is accentuated by the presence of water. Two mechanisms by which water may find itself on the rock face are by driving rain and water condensation. A model developed by Lyons[1] has been used to assess temperatures within the micro-environment. In conjunction with the comparative use of climatological data from nearby Cue, the model was unable to predict dew-point temperatures on the rock face at any stage, with the site environment as it

currently exists. The effects of revegetation were then modelled and shown to be most unlikely to lead to condensation on the rock surface by dew formation or fog inception.

The model's findings are accepted with reasonable confidence and it seems that the primary weathering mechanisms may be through driving rain. A suggested management plan has been drawn up that should protect the art from rain, and yet minimise the effect of humidity. It is noted that any management plan must be assessed continuously and that further monitoring of the air is essential.

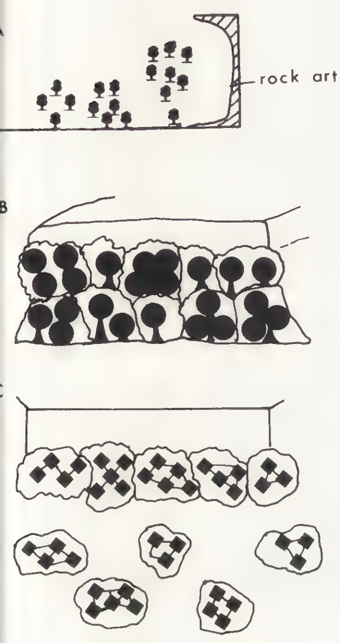

Fig. 10: a) cross-sectional view of proposed planting in front of rock art.

Fig. 10: b) side view - looking into the shelter.

Fig. 10: c) aerial view - note the arrangement for the vegetation.

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Acknowledgements

We would like to thank John Clarke and Tom Lyons for their helpful discussions, and staff of the Museum's Department of Aboriginal Sites for their help and co-operation.

Special thanks go to Lucy Marchesani for her patience in typing this manuscript.

METHODOLOGIE D'ETUDE DES ABRIS SOUS ROCHE ORNES EN CLIMAT TEMPERE - CAS DE L'ABRI DE LA CHAIRE A CALVIN (FRANCE)

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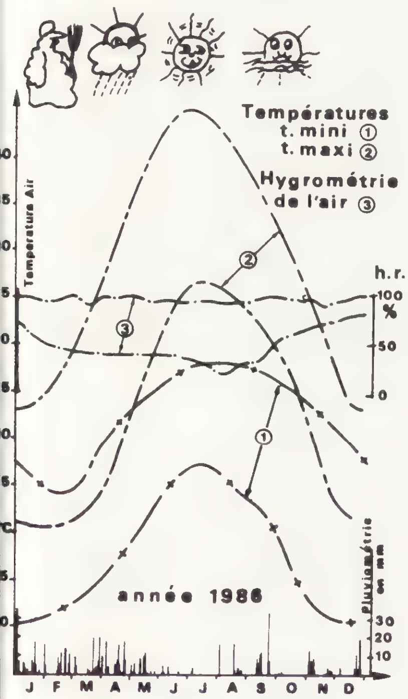
ESUME

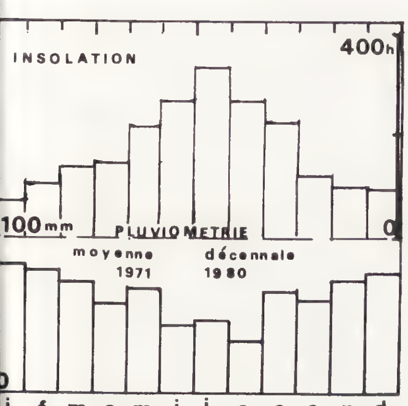
a recherche sur la conservation les oeuvres préhistoriques dans le lomaine de l'art de plein air l'est pas aussi avancée en France que celle appliquée à l'art des avernes.

Notre groupe de travail met au oint un processus analytique mul- iparamétrique pour suivre la phé- noménologie dynamique naturelle et elle héritée de l'activité humai- ne en vue d'apporter des remèdes concrets.

Nous présentons ici les résultats préliminaires acquis sur un site ravé soumis à l'influence du cli- mat de type tempéré à dominante océanique.



ig. n° 1 : Caractéristiques ther- iques pluviométriques dans le épartement de la Charente (station e La Couronne).



ig. n° 2 : Evolution annuelle de a pluviométrie et de l'insolation station de La Couronne).

Introduction

En France les abris sous roche sont très nombreux le long des flancs des vallées creusées dans les calcaires, les calcaires gréseux et les grés, mais ceux qui recèlent encore une oeuvre préhistorique sont rares. C'est la raison pour laquelle notre expérience est relativement réduite comparée à celle que nous avons pu acquérir dans le cas des grottes(1).

Nous avons donc décidé d'élaborer un modèle d'enquête en vue de pouvoir constituer un fichier analytique de données, en prévision de l'étude conservatoire des oeuvres pariétales sous abris, sur la base d'une recherche méthodologique fondamentale.

A l'époque paléolithique et plus récemment, les peintres préhistoriques ont sans doute exercé leur art sur les parois des abris de plein air comme ils l'ont fait avec beaucoup de talent dans les grottes dont certaines ont acquis une renommée mondiale.

Si les parois rocheuses ont été recouvertes par les peintures, ces dernières ont presque toutes disparu dans notre pays, alors qu'elles sont encore plus ou moins bien visibles dans la région de la Valltorta en Espagne du Nord-Est(2), au Sahara(1) et en Australie, bien sûr(3)-(4).

La cause essentielle de cette disparition quasi-totale des peintures est liée essentiellement à l'action directe du climat aérien (chaleur, froid, gel, humidité, ensoleillement, développement de bactéries, de mousses etc...) qui a provoqué la dégradation du support rocheux (boursouflures, écaillages etc...) et le gommage des traits et des surfaces colorées.

La France est soumise au climat de type tempéré. C'est un climat composé de quatre saisons, chacune étant marquée par des paramètres contrastés comme l'indiquent les figures n° 1 et 2.

Ainsi, et pour tout ce qui concerne l'époque paléolithique, le patrimoine national attaché aux abris sous roche est de ce fait seulement constitué de gravures et de sculptures.

Parmi les sites les plus importants quant à la qualité artistique de l'oeuvre préhistorique, nous citerons celui de la "Chaire à Calvin". Il se trouve dans la commune de Mouthiers - département de la Charente. (France de l'Ouest - cf. fig. n° 3). Voir ci-après.

Sa situation géographique est la suivante :
- 45°35' de latitude Nord
- 0° 5' de longitude Est.

Pour les autres informations, le lecteur se reportera au tableau n° 1.

Cette note est présentée alors que la collecte des données se poursuit encore. Nous ne produirons donc ici que des résultats provisoires. Ceux-ci sont intéressants et nous incitent à suivre le maximum de paramètres afin de bien individualiser l'impact de chacune des saisons préventivement à toute action conservatoire.

L'exposé est présenté sous la forme de fiches. Pour chacune d'elles, nous précisons la nature de l'information qu'elle contient et les résultats acquis.

CARACTERISTIQUES GENERALES DE L'ABRI

Localisation : x = 426,60 y = 64,15 z = +170,5 m
Feuille de : ANGOULEME n° 5-6 - commune de : MOUTHIERS-sur-BOEME
ouverture de l'auvent = 12 m
profondeur depuis l'entrée = 8,0 m
hauteur du plafond = 4,15 m au maximum - 1,50 m à la hauteur de la frise
frise ornée = 3 m de long - 0,65 m de haut maximum
vient en plus une tête de 0,20x0,14 m (félin(5) ou cheval sculpté à l'envers(6)), à 1,20 m à gauche.
L'abri est associé à un gisement paléolithique connu avant 1866.
Découverte de la frise en 1927. Elle était masquée par les dépôts préhistoriques.
âge des dépôts = Magdalénien.
Altimétrie :

Rivière	Fond de vallée	Plancher abri	Toit de l'abri	Sommet falaise	Sommet colline
+67 m	+68 m	+70,5 m	+74,65 m	+80 m	+113 m

TABLEAU N° 1

1. Fiche relative à la situation géographique et à l'environnement
Son rôle est de mentionner l'état géographique et la topographie des lieux, complétés par un historique de l'état de l'environnement. En effet le cadre naturel évolue avec les saisons d'une part, avec le temps d'autre part.

Fig. n° 3 : Carte de localisation.

Ces changements peuvent avoir des retombées directes et indirectes importantes sur l'état présent de dégradation du site et des oeuvres d'une part, sur la vitesse de cette dégradation d'autre part.

Concrètement, le creusement de l'abri à la base de la falaise résulte de l'action conjuguée des mécanismes d'érosion tels que ruissellement, action du gel, effondrements etc... L'abri est distant du petit ruisseau dit "le Gersac" de 25 m environ. Le plancher de l'abri est à 2,50 m au-dessus du cours d'eau.

La falaise est orientée vers le Sud-Est, ce qui signifie que le soleil éclaire directement dès le matin la partie inférieure de l'abri. De ce fait, il apparait à partir de 08 h en été et entre 10 h et 10 h 30 en hiver. L'après-midi l'éclairage direct disparaît totalement à partir de 16 h en été et à partir de 15 h en hiver (cf. fig. n° 4).

De grands arbres constituent un écran partiel au printemps et en été.

Ces arbres perdent leurs feuilles en automne et il n'y a plus d'écran naturel entre novembre et fin avril l'année suivante, soit pendant 6 mois.

La falaise limite un plateau dont la pente topographique est faible et dirigée vers le ruisseau (cf. fig. n° 5). Il y a plusieurs siècles, ce plateau était couvert de forêts. Il y a un siècle environ une grande surface a été déboisée et mise en cultures (blé - luzerne etc...). Au fond de la vallée il y a beaucoup de prairies et de sources.

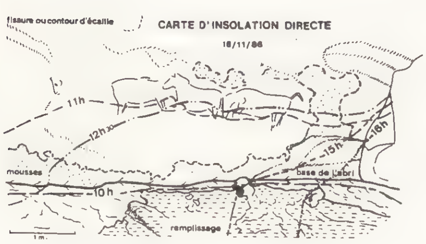


Fig. n° 4 : Carte de l'insolation directe de l'abri en automne.

2. Fiche relative au cadre géologique
Il est important de connaître la nature exacte des roches qui constituent l'abri. Les paramètres que nous réunissons ici sont d'ordre descriptif et quantitatif.

La roche est étudiée à l'échelle régionale (origine, âge, géométrie des couches, fracturation, fossiles) et à l'échelle locale (géomorphologie, faciès, constituants, altération etc...). On cherche ensuite à connaître les caractéristiques pétrophysiques (porosité, perméabilité, microfracturation etc...).

Ce sont des paramètres qui varient en fonction de l'environnement climatique, hydrogéologique et chimique (dissolution).

Ici la falaise et l'abri ont été creusés par le cours d'eau dans les calcaires du Turonien (Crétacé supérieur).

L'analyse pétrographique est en cours. Nous avons pu différencier trois couches superposées et différentes les unes des autres par leur morphologie, leur couleur, leur nature, leur compacité.

A la base, le calcaire est constitué de couches épaisses ; il est blanc gris et cristallisé. A droite de l'abri, la paroi est lisse, c'est là où est sculpté le bas-relief.

A gauche de l'abri le calcaire est criblé de trous ; ce sont les fossiles qui ont disparu par actions mécaniques (érosion) et chimiques conjuguées (dissolution).

Dans la partie médiane, on observe des calcaires cristallins riches en fossiles, blancs, avec des couches minces.

Dans la partie supérieure, on trouve des calcaires gris, tendres, un peu argileux (calcaires marneux).

La succession des couches est donnée sur le dessin de la figure n° 6.(cf.ci-ap.).

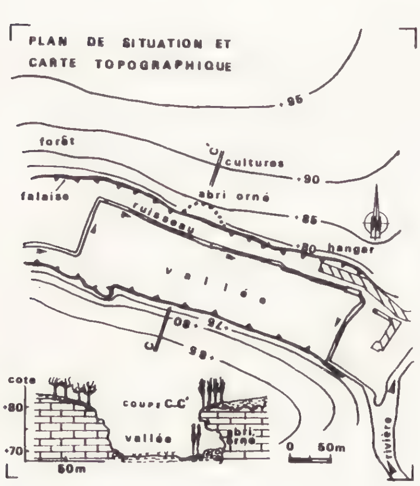


Fig. n° 5 : Géomorphologie des environs de l'abri.

Dans le détail, l'abri est creusé dans la partie inférieure du dépôt. L'homme préhistorique a choisi un banc dur, à paroi lisse et légèrement inclinée, pour sculpter la magnifique frise comportant un ensemble composé d'un bovidé et de trois équidés (cf. 3 et 4 déjà cités et planche n° 7). on notera à ce propos que des traces de peintures ont été identifiées en 1927. Elles ont disparu aujourd'hui. (cf. ci-après).

3. Fiche de l'état de la paroi ornée
Sur cette fiche nous reportons toutes les données relatives à la géomorphologie et à la nature minéralogique, pétrographique et biologique de l'interface air-paroi.

L'utilisation de la photographie stéréoscopique, de la macrophotographie stéréoscopique complétée par l'observation in situ, permet la surveillance de phénomènes évolutifs liés à la "vie" de la paroi ornée. Nous citerons parmi une longue liste : l'écaillage - la fissuration - la corrosion - l'accroissement ou l'ablation d'enduits, de croûtes, de patines, d'efflorescences cristallines etc.

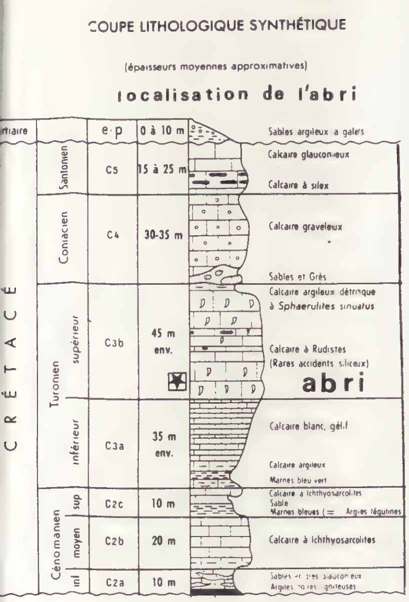


Fig. n° 6 : Log lithologique vertical des couches de terrain.

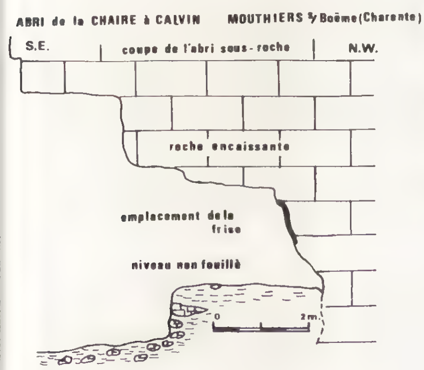
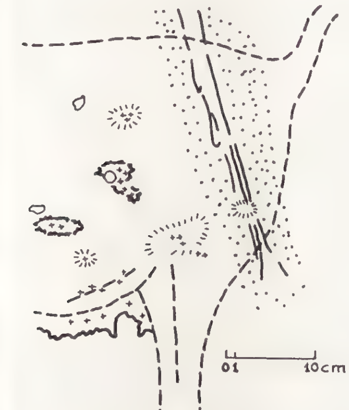


Fig. n° 7 : Coupe verticale de l'abri.



- Trait gravé
- Calcification en "nappe"
- Micro-calcification
- "Coulée" de calcite
- Ecaille ancienne (imputable à la gravure du trait)
- Ecaille
- Micro-dépression

Fig. n° 8 : Géomorphologie pariétale (détail partie droite).

Le procédé évoqué ci-dessus offre la possibilité d'appréhender l'évolution d'une plage de dimensions déterminées en introduisant la notion du relief.

Cela met en évidence toute une série d'informations et de détails qui, habituellement, sont "masqués" lors de prises de vues classiques (cf. photo n° 1). L'appareil photographique utilisé : NIKKORMAT 24 x 36 doté d'un objectif micro-Nikkor de 55 mm de focale est placé sur une platine spécialement usinée qui est solidaire d'un ensemble métallique articulé en forme de tripode rigide solidement fixé au sol. Sur la platine, une réglette graduée au millimètre permet, en fonction de l'objectif et de la distance à la paroi surveillée, de connaître le déplacement latéral à apporter au centre de l'appareil photographique pour obtenir le recouvrement nécessaire à la réalisation de couples stéréoscopiques.

Photo n° 1 : Vue générale sur la frise gravée.

Concrètement, l'étude que nous avons débutée en juillet 1986 nous a permis de localiser les surfaces où il y a :
- un interface : calcaire-air,
- un interface : calcite-air,
- un interface : mousse-air,
- un interface : fougère-air etc...

Dans le cas présent, nous donnons un détail sur la partie droite de la frise gravée (cf. fig. n° 8).

L'épaisseur de la couche de calcite atteint au maximum jusqu'à 4 mm. Elle masque les détails de la sculpture dans certains endroits.

Ces dépôts proviennent de l'action dissolvante de l'eau souterraine qui laisse précipiter le $Ca\ CO_3$ sur la paroi au contact avec l'air.

Ce phénomène nous amène à suivre tous les paramètres (climat - eaux - calcite) durant une année au moins, pour contrôler la dynamique physico-chimique qui tend à couvrir les gravures.

4. Fiches climatologiques et hydrogéologiques
Nous devons suivre en permanence et avec beaucoup d'attention, le cycle de l'eau (eau de pluie, eau souterraine, eau d'émergence) car dans les pays à climat tempéré, cet élément joue un rôle capital et plus particulièrement dans la destruction des oeuvres préhistoriques.

Nous utilisons les informations d'une station météorologique où sont enregistrés : la pluie, la neige, les vents, l'hygrométrie et la température de l'air extérieur ; sur place nous enregistrons la température et l'hygrométrie dans l'abri, les écoulements d'eau de suintement qui émergent par la voûte et le long des parois. Nous mesurons également les teneurs en eau à l'intérieur de la roche calcaire.

Tous ces paramètres sont réunis soit :
sur des tableaux, soit sur des diagrammes, soit sur des cartes.

Nous allons donner quelques exemples ci-après et compléter les dessins par un commentaire approprié.

4.1. Analyse thermique
Les mesures de température de la roche sont obtenues par application d'une sonde sur la paroi. Les valeurs lues sont reportées sur un calque superposé à une photographie, selon un quadrillage préétabli et adapté à chaque site. Dans un deuxième temps, les mesures sont transcrites sur une carte simplifiée où ne sont dessinés que les principaux traits géomorphologiques du support naturel.

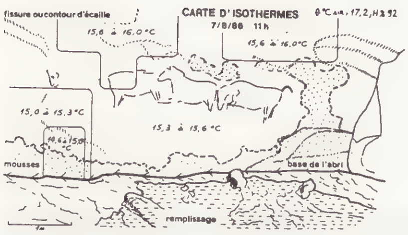


Fig. n° 9 : Températures de surface de la partie ornée de l'abri.

La construction de cartes représentatives d'un instant donné est établie après que soit déterminé le pas de découpage thermique le plus représentatif (0,1°C ou (x) - 0,5°C ou (x) préalablement au tracé des isothermes.

La mesure est répétitive :
- au sein d'une journée à l'échelle de 6 heures
- au sein de la saison à l'échelle de 2 mois.

Dans le premier cas, il s'agit de saisir la phénoménologie "instantanée" et/ou "rapide" imposée par l'atmosphère.

Dans le second cas il s'agit d'observer les effets retardés qui s'exercent au sein du support et de l'environnement souterrain.

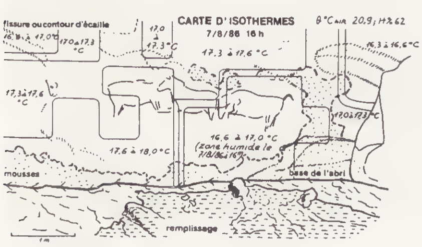


Fig. n° 10 : Températures de surface de la partie ornée de l'abri.

Les exemples que nous avons choisis (cf. figures n° 9 et 10) correspondent à l'état thermique de la paroi le 7 août 1986 à 11 h et à 16 h. Ils révèlent la réaction de l'interface air-roche aux effets de l'ensoleillement diffus et des ombres portées en période estivale.

On remarquera :
- que la valeur absolue des températures de surface croît entre 11 et 16 h mais que l'écart (Δt) entre les mesures extrêmes reste le même (Δ = 1,4°C) entre 11 h et 16 h,
- l'absence de gradient,
- l'effet limité de l'impact hydrogéologique en raison de la rareté des arrivées d'eau à cette saison (cf. ci-après 4.2.).

4.2. Analyse hydrogéologique
Il s'agit de connaître les modalités d'infiltration des eaux de pluie à travers le sol et le calcaire fissuré, la localisation et la pérennité des émergences dans l'abri, le régime des circulations et les retards entre le moment où l'eau de pluie tombe sur le plateau et celui où elle ressort à la voûte et/ou sur la paroi.

Il est important d'étudier également la composition chimique de l'eau (gaz dissous et cortège ionique).

Ainsi, après 6 mois d'étude nous avons pu constater :
- que les émergences les plus nombreuses se situaient à la voûte de l'abri,
- qu'au mois de juin les sculptures étaient recouvertes en partie seulement par les eaux de suintement qui émergent au-dessus des animaux sculptés (cf. fig. n° 11).

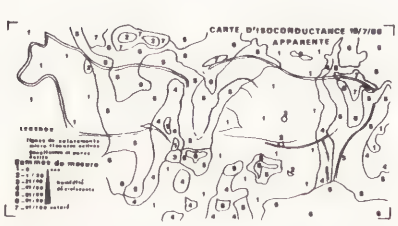


Fig. n° 11 : Etude des suintements sur la frise sculptée.

En été 1986 il y a eu dans le Sud-Ouest de la France une longue sècheresse qui s'est prolongée entre juillet et novembre.

La paroi s'est asséchée peu à peu et nous avons suivi le phénomène en faisant un grand nombre de mesures électriques. Nous avons établi des cartes d'isoconductivité de la paroi. Nous avons choisi un exemple qui correspond au maximum de la sècheresse (cf. fig. n° 12). On remarque que toutes les parois sont désaturées.

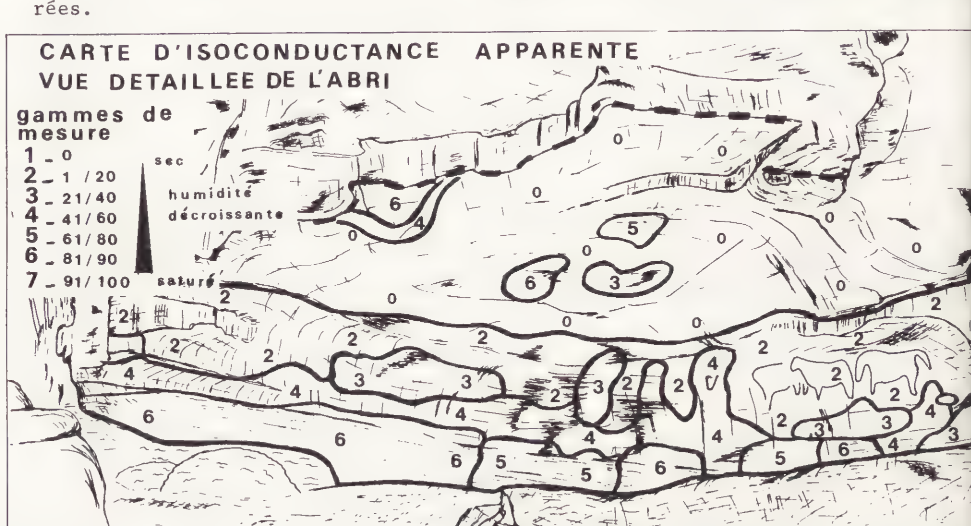


Fig. n° 12 : Carte d'isoconductance de la paroi de l'abri.

L'eau suinte en quelques points particuliers. Ceux-ci sont situés au-dessus de la frise. Ces zones humides permettent aux mousses et aux lichens de subsister.

C'est la comparaison chiffrée de telles cartes établies tous les deux mois qui sera intéressante pour comprendre le phénomène et agir dans le cas d'une humidité excessive ou d'une sècheresse trop forte.

Bilan

Les résultats mentionnés ici constituent une première étape vers l'élaboration de modèles d'études des impacts du climat, de l'homme et de l'environnement actuels mais également passés :
- sur l'évolution pariétale d'une part,
- sur l'état de conservation actuelle des oeuvres préhistoriques inscrites dans les abris sous roche d'autre part.

L'exemple que nous présentons ici s'applique au cas d'un site soumis aux actions multiples du climat tempéré.

Cette étude en cours, nous permet à la fois :
- de transposer les méthodes d'approche déjà existantes,
- d'affiner le modèle de stockage des données, déjà rodé dans le cas des grottes ornées (cf. fig. n° 13), - voir page ci-après,
- et de mettre au point de nouvelles technologies.

Nous insistons en particulier sur l'intérêt qu'il y a à développer la cartographie thématique répétitive afin d'affiner l'étude des relations de cause à effet multiparamétriques.

Nos connaissances sur le fonctionnement de ces systèmes intéractifs sont complexes et restent encore trop fragmentaires. Des lacunes doivent être comblées en particulier dans les domaines de la physique, de la chimie et de la biologie.

C'est par l'amélioration méthodologique et conceptuelle et par la multiplication des cas d'études que passe l'avancement de la recherche fondamentale et appliquée au domaine de l'art de plein air.

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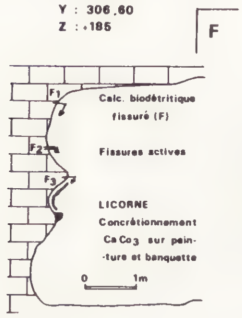
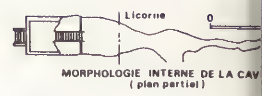
LASCAUX - GROTTE

Cne : Montignac
Flle I.G.N. : Terasson 5-6

Ech : 1/25 000e
X : 508,30
Y : 306,60
Z : +185

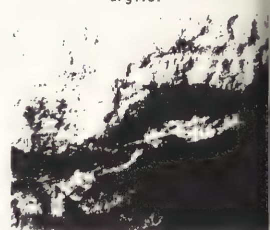
FICHE ETALON



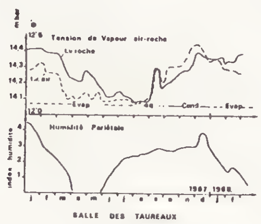


COLORANTS :

noir = manganèse Mn O_2
rouge = oxyde ferrique associ argile.



ETAT ANNUEL DE L'INTERFACE AIR-ROCHE						
	1974	1975	1976	1977	1978	1979
Evaporation Nombre de jours	277	247	283	311	303	167
Equilibre air-roche	88	112	72	54	62	190
Condensation	0	5	8	0	0	8



CONCRETIONNEMENT PARIETAL
support pré-pictural : roche nue (p.p.),
croûte calcique semi-transparente et enchevêtrement micro-cristallin
Evolution après découverte - 1940 :
. croissance polymorphique ponctuelle (baguettes)
. voile amorphe sur encolure et autres écailles hydrogéologiquement actives.

OBSERVATIONS :

Diagnostic : la présente figure su depuis l'aménagement de la grotte agression naturelle localisée, lent précipitation discontinue sur écail CO_3Ca sous forme d'un voile amorphe, blanc. Ce phénomène peut être contr par des chutes et/ou disparitions (par eau agressive) de microéléments périphériques.

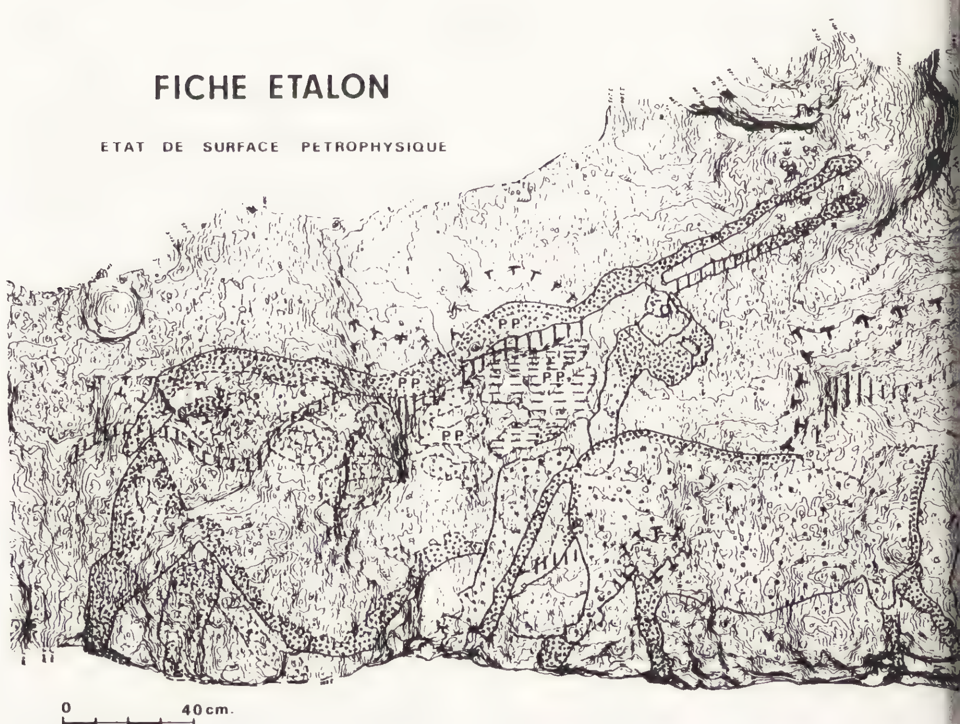
Intervention : l'ablation du dépôt mal ancré est possible par intervention hydrique et micr canique pour en limiter l'extention.

Bilan : concrétionnement chronique, localisé, arythmé - A surveiller pour action curative t nalle ou quinquenalle avant ancrage du voile sur roche.

- Fiche étalon. Recto.

FICHE ETALON

ETAT DE SURFACE PETROPHYSIQUE



Mn dense -appliqué par tracé épais lessivé (p.p.)

Mn léger -par soufflage

ocre rouge -par tracé épais-lessivé (p..p.)

surface rocheuse à nue (écaille)

surface calcifiée (cristaux), ancienne

surface calcifiée amorphe; récente (depui

- Fiche étalon. Verso.

Fig. n° 13 : Modèle de fichier scientifique et technique - Cas de la grotte de Lascaux.

Working Group 25

Control of Biodeterioration

Contrôle de la biodétérioration

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CONTROL OF BIODETERIORATION, TRIENNIAL OVERVIEW

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PROGRAMME FOR 1985 - 1987

1. Information/Literature; gathering, evaluating, abstracting and distributing.

2. Prevention; design, maintenance, environmental considerations, monitoring and documentation.

3. Treatment; chemical and non-chemical.

4. Effects; of treatments on artifacts and associated material.

5. Health and Safety; toxicity and hazards.

6. Causes and Mechanisms; identification of organisms and information on why the problem exists and how organisms effect collections.

SUMMARY

The initial three years of the group were spent on establishing a network of people working on, or interested in, the topic of Biodeterioration. All working members were asked to submit summaries of work underway and this information has been collected by the Smithsonian Institute. Packages containing summaries were circulated to all working members and as a result various members have been in contact with each other sharing information and experiences.

Interesting projects underway deal with treatments using a variety of chemical and non-chemical methods. Ongoing research for safe and effective biocides continues and headway is being reported. Freezing, which seems to be a very satisfactory and safe method of dealing with insect infestations, if carried out properly, is receiving a lot of attention and results are promising. On the prevention front some very important work in the area of maintenance, monitoring and documentation has been carried out with encouraging results. New findings of biocide deposits in collections, which creates incredible health hazards, are alarming. Detrimental effects of some biocides on art and artifacts have always been suspected and often talked about but recently they have been dramatically illustrated and documented.

Important research into the habits and biology of pests is ongoing and other interesting projects such as research into traditional techniques of treatment or the use of gamma irradiation as a control method are examples of the broad range of research and work underway in the many areas of Control of Biodeterioration.

ON THE FOXING-CAUSING FUNGI

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SUMMARY

'oxing is a deterioration found on paper objects. ince the author succeeded n making fungi grow on oxing, he is now studying he causes and mechanisms of oxing in order to contri-ute to the conservation and restoration of paper art-vorks and archives.
fter incubating samples of oxing in a Conway's unit hose water activities were regulated to 0.94 and 0.84 t 25°C for 7 to 30 days respectively, 25 strains of ungi were isolated from the oxed areas. Growing onidiophores and conidia of ungi were observed on the ncubated samples of foxing y scanning electron micro-scope. According to the vater activity of each strain, these strains could e divided into two groups: 7 strains of absolute tono-hilic fungi and the others of facultative tonophilic ungi. Only the former roup made brown spots and roduced malic acid 5-9 imes more than the latter roup. The seven strains of bsolute tonophilic fungi vere identified as 4 strains f Aspergillus penicilloides pegazzini and 3 strains of urotium herbariorum Wigger: Fr.) Link. The uthor considers that the ain causes of foxing are hese and related species.

Introduction

It is a well-known fact that brown spots appear on paintings drawn and books printed on papers. This is called "foxing" and restoration works must be done when it is found on paintings and books, since it devalues the art objects in question. Furthermore, it is not possible to draw on paper which has already been foxed. Western researchers have been interested in foxing and have studied it for fifty years or more. However, the causes of foxing have not yet been made clear although several opinions can be found for them.
The author received, for the first time in 1974, information on "foxing". He has had an interest in this problem since then, and has been collecting foxed papers and experimenting on foxing. After he received, in 1982, a foxing sample found on the replica of decorative paintings on hemp papers inside the main building of Byōdōin Temple, he discovered, by incubating a piece of this foxing sample at Aw 0.94 or 0.84 at 25°C, that fungi grow only on foxed areas. The author is now studying the causes and mechanisms of foxing with this clue to go upon.

Materials and Methods

(1) Some causes of foxing may be related to the appearance of foxing on paper. For this experiment, the author collected two kinds of samples of foxing caused by two different factors, fungi and iron.

(2) Observation by scanning electron microscope was carried out by JSM-50A and JSM-T330 (hereafter referred to as SEM), and elemental analysis of X-ray was conducted by energy dispersive spectrometer Link-Q200J (hereafter referred to as EDS). Specimen paper of the foxed area was cut into 5 mm square pieces and mounted on specimen stabs with carbon paint. SEM observation and elemental analysis of the specimen were done after vacuum evaporation with carbon.

(3) A piece of foxing samples was set in a Conway's unit regulated at Aw 0.94 or 0.84, and incubated at 25°C for 7 or 30 days.

(4) In this experiment, 25 strains of fungi were isolated from foxed areas.

(5) Water activities(referred to as Aw) of the used strains were measured at Aw 1.00, 0.94, 0.84, 0.75, 0.65 and 0.55.

(6) Organic acids of the 25 strains and foxed areas were analysed by isotachophoresis.

Results

After several kinds of paper collected as samples of foxing were incubated at Aw 0.94 and 0.84, 25°C for 7 or 30 days, the author isolated and purified 25 strains of fungi growing only on the foxed areas. He has been studying the causes and machanisms of foxing with these strains, and the following results have been obtained.

(1) When the sample of foxing on hemp paper was kept at Aw 0.94, 25°C for 4-7 days and at Aw 0.84, 25°C for 25-30 days, fungi grew only on the foxed areas and were not found on the white areas. Though the SEM image of the foxed areas on hemp paper showed many mycelia and conidia on and around the fibers of hemp paper, only beautiful fibers of hemp paper were observed and contamination by fungi was not seen in the SEM image of the white area. These SEM images suggest a close relationship between fungi and the formation of foxing. Moreover, the SEM image of the foxed areas on hemp paper incubated at Aw 0.84, 25°C for 30 days showed conidiophores of fungal growth and increasing fresh conidia on the fibers (Fig.1).

ig. 1: A SEM image of oxed areas on hemp paper ncubated at Aw 0.84, 25°C or 30 days: conidiophores nd conidia of Aspergillus eniciloides.

On the other hand, since there is an opinion that the formation of foxing is related to iron; the existence of iron was confirmed by EDS for the foxed areas of hemp paper. Because iron, zinc and copper could not be found by an elemental analysis of EDS, the author considers from these results that foxing on hemp paper is formed by the action of fungi(Fig.2).
There have been some researches made that suggest that foxing may be formed by irons in and on papers. The author was able to

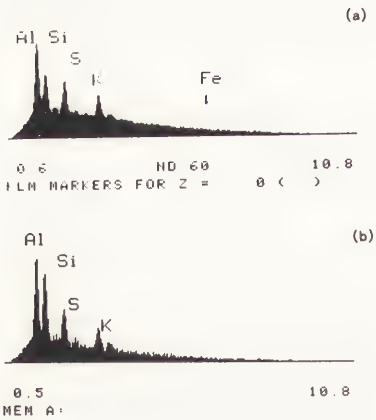

Fig. 2: X-ray analysis of foxing caused by fungi on hemp paper: (a) foxed area, (b) white area.

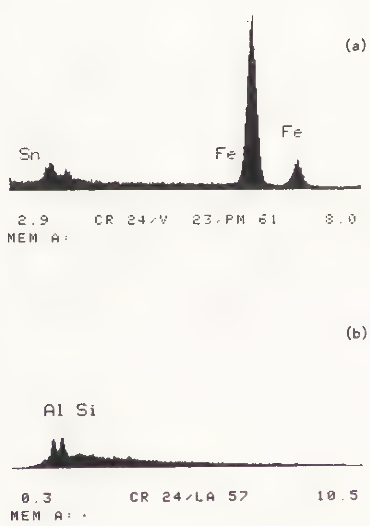

Fig. 3: X-ray analysis of foxing caused by iron on pulp paper: (a) foxed area, (b) white area.

collect a sample of foxing caused by iron but, when secondary electron images were compared, it was impossible to differentiate which is the foxed area and which is the white area of this samples. However,reflective electron images differentiated clearly the foxed area and the white area of this sample. Elemental analysis of the foxed area of this sample by EDS detected a large amount of iron and a small amount of tin (Fig. 3). This proved that the iron was plated with tin.

(2) The water activities of the 25 strains were measured. These fungi were divided into 2 groups: 7 strains belonged to the absolute tonophilic fungi whose growing condition is Aw$<$1.00, and the other 18 strains belonged to the facultative tonophilic fungi whose growing condition is Aw$\leqq$1.00. A climograph of each strain was made, based on the measurement of the water activities and the temperatures for growth.

(3) After the 25 strains were reinoculated on hemp paper, these papers were incubated at Aw 0.94, 25°C for 5 weeks. Foxing could only be made on the 7 inoculated strains of the absolute tonophilic fungi. It was not possible to make foxing on paper with the other 18 strains.

(4) Organic acids of the 25 strains were analysed by isotachophoresis as a metabolite. These strains produced malic acid, fumalic acid, lactic acid and acetic acid. The production of malic acid was especially noticeable on the 7 strains of the absolute tonophilic fungi. These strains metabolited 5-9 times more malic acid than the other 18 strains of the facultative tonophilic fungi.
On the other hand, organic acids in the extracts of the foxed area were also analysed. These extracts showed similar components of organic acids produced by the 7 strains of the absolute tonophilic fungi. A larger amount of malic acid could also be found than with the other organic acids. Therefore, since analyses on organic acids in the metabolites of the 7 strains coincided with the results of foxed areas, it is assumed that malic acid may be related to the formation of foxing by some reactions.

(5) The 7 strains belonging to the absolute tonophilic fungi isolated from foxings were identified as follows:

a) 4 strains: Aspergillus penicilloides Spegazzini

b) 3 strains: Eurotium herbariorum (Wigger: Fr.) Link

These strains are considered as the foxing-causing fungi, according to the results above mentioned.

Discussion

(1) Appearance of foxing on hemp paper: Replica of decorative paintings at the Hōōdō in Byōdōin Temple, which was constructed in 1053, were painted on hemp paper from 1955 to 1962 by the artist Tsunekichi Koba and others (hereafter referred to as hemp paper). Although 60 artworks on hemp paper have been stored and exhibited in the treasury building of the Temple since 1972, it is said that foxing was found remarkably on them since about 1977 and thier restoration work was carried out in 1982. The author received a piece of the hemp paper.

(2) Environment of the replica preserved in the treasury building of Byōdōin Temple: The replica of decorative paintings on hemp paper have been preserved and exhibited in the treasury building since 1972, but began to show marked foxing five years later. Since it was necessary to know in what kind of environment these replica had been preserved for 5 years, a record of the temperature and humidity in the treasury building of the Temple were taken for a year from April, 1983 to March, 1984. This record showed that the treasury building reached 70-80% in relative humidity and 20-30°C in temperature during the three months from July to September. The climograph of the foxing-causing fungi showed that the optimum humidity and temperature of their growth were Aw 0.75-0.94 (equal to 75-94% RH) and 25-35°C. Therefore, the environment of the treasury building was in the best condition for the growth of the foxing-causing fungi during these three months.

(3) On the nutrients for the foxing-causing fungi: When some materials are damaged by microorganisms, there is a tendency in general to consider that microorganisms grow on some nutrients of the materials. To be sure, wood rotting fungi grow with the degradation of cellulose and lignin in woods and major bacteria putrefy with the degradation of proteins and others. However, not all microorganisms grow with assimilation of nutrients which are produced by the degradation of the substrates.
Airborne microorganisms and microdust always exist on every material, including paper, and the absolute tonophilic fungi like the foxing-causing fungi are able to germinate by their own

nutrients in spores in spite of there being no nutrients around them, if environments of temperature and humidity provide optimum conditions. However, since the nutrients in spores are limited, growth is stopped immediately after making spores, if the germinated hyphae can not find any nutrients. When the hyphae are able to meet microdust, they will grow with vigor. On the surface of paper and others, dust exists as invisible and microscopic particles. Therefore, the foxing-causing fungi do not spread all over the surface of the paper, but only grow as colonies 2-5 mm in diameter. The growth then stops, because they must utilize the microparticles of dust as their nutrients. This, it is reasonable to consider, is the reason why the foxing-causing fungi make brown spots.

(4) Control method of foxing in Byōdōin Temple: It is clear that the foxing-causing fungi cannot grow in an environment below Aw 0.70 as was seen from their climographs. In general, though air conditioning is utilized in controlling temperature and humidity in large spaces of buildings, it is very difficult to operate 24 hours. Since the water activity of the treasury building is below Aw 0.70 (equal to 70% RH) except from July to September, the author considered that the appearance of foxing would be prevented if the relative humidity in the building could be kept below 70% RH during these three months. For this reason, the author recommended setting up a dehumidifier that has a capacity of keeping the relative humidity below 70% from July to September.

Conclusion

Studies on foxing have been accelerating after fungi were isolated from foxed areas of hemp paper. Researches on various aspects of foxing such as identification of the fungi, analysis of organic acids in the extracts from foxing and in the metabolites of the foxing-causing fungi and so on are being made. As the author considers that one of the main causes of foxing is fungi, he hopes to make clear the formation mechanisms of foxing and to contribute to the restoration of paintings and archives.

NOTES

1. H. Arai, "Microbiological Studies on the Conservation of Paper and Related Cultural Properties, (Part 1) Isolation of fungi from foxing on paper," Science for Conservation 23 (1984): pp. 33-39.

2. H. Arai, "Microbiological Studies on the Conservation of Paper and Related Cultural Properties, (Part 2) Physiological and morphological characteristics of fungi isolated from foxing, foxing formation mechanisms and countermeasures," Science for Conservation 26 (1987): in press.

METHODOLOGY USED IN INSECT PEST SURVEYS IN MUSEUM BUILDINGS - A CASE HISTORY

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SUMMARY

Methodology used in insect surveys of museum buildings is presented. Insect surveys of the Curatorial Tower (storage of collections and office space) 13 floors each 10,000 sq', the Curatorial Tower outer stairwells which are not heated and the Ellery Street Warehouse (approx. 20,000 sq') were undertaken to gather information for assessing the insect problem, and establishing methodology and staff involvement for future monitoring and surveys. Four surveys of the collection building were undertaken . The first survey was undertaken to design the methodology and to remove all insects to a zero point for further surveys. The Curatorial Tower has a continuous bank of east, south, and west facing windows which were found to act as insect traps for phototaxic insects. Floor plans showing the windows were used to survey the building
The other three surveys, were done over a period of two months. The data was tabulated. It was possible to illustrate insect population size, distribution and fluctuation according to window, floor and two dimensionally by window/floor. Analysis of the charts lead to an assessment of the insect problem. The survey method used for the large one floor warehouse was sampling dust and cobwebs at specified locations recorded on a floor plan. Analysis of the sampled showed the presence of insect remains and the precise location of an active infestation was located easily in the large area.
Dust samples taken from window sills were used to survey the unheated stairwells of the collection building. The dust samples were recorded according to window location. Analysis of the dust showed a diffuse pattern of insects and a small concentration of moth remains and larval moults at a specific location which was shown to be the source of moths reported alive some months prior to the survey. These methods of insect pest survey were designed for a specific museum but they have a more general application.

1. Introduction

Each museum is unique. The methodology used in this project may not be appropriate for other museums. But our experiences may assist others in designing methods of surveys for assessment of the insect pest problem for their own museum.

The project was undertaken to determine the presence or extent of an insect problem in the Museum buildings and suggest a management program for preventative insect pest control. The final report was an 80 page document. Prior to this project which started Jan 27/86, insect pest control had been undertaken on a passive level, waiting for the insect to appear and then responding. The need for the assessment of the insect pest probelm became apparent when a minor insect outbreak occured, and in response, neither staff responsibilities nor the appropriate method of control were clearly defined because of the lack of thorough knowledge of the problem.

The project began by eradication of the active insect infestations and establishing a diary of events. At the same time, insect surveys of the Curatorial Tower (Collections) 13 floors each 10,000 sq', and the outer stairwells which are not heated, the Ellery Street Warehouse (approx. 20.000 sq') and parts of the Exhibit Building were undertaken to gather information for assessing the insect problem, and establishing methodology and staff involvement for future monitoring and surveys.

It is the methodology of the surveys and selected example of the interpretation of the results which will be presented in this paper The project was extensive, covering a time span of a year and covering extensive areas as described above.

The final recommendations were to implement an integrated systems approach to insect pest control and to develop a manual with pertinent information on treatments, and salient information on the identification and the biology of the significant insect pests.

2. Insect Pest Surveys of Curatorial Tower (Collections Building)

2.1 Methodology

Four insect pest surveys were undertaken. The initial survey focused on the collections and the building. The purpose of the initial survey was to: familiarize the author with the collections; collection areas; the building; and the staff responsible for the care of the collections; and to design procedures for future surveys.

The following three surveys focused on the building itself, for the main purpose of assessing the insect problem in the Curatorial Tower.

Initial Survey

Purpose and procedures.
In the initial survey a diary was kept for recording occurrence, location, species, etc. of the insects and insect remains in the collection areas and the window sills of the building.
The insects were placed in glassine envelopes on which was marked the location date, and immediately frozen for at least 48 hours at -20°C. They were then identified.

The numbers of insects was not important at this time. The main value of collecting all the insects was to have a zero point for the future surveys. In this specific building (Curatorial Tower), the west, south and east side of the building have a continous row of windows which are in offices adjacent to collection areas and in collection areas. It was apparent that the windows act as light traps for phototaxic insects, which included all the above insects except moths.

The method of just recording information in a diary, used in this survey was awkward and difficult to interpret. Thus it was obvious that there was a need for a floor plan and a check list for recording for future surveys. Floor plans were designed for ease and accurateness of checking and recording the presence and location of the insects.

During the initial survey several problems arose: inaccessible collection areas; clarification of responsibilities; and most important a need for procedures for permanent recording and documenting of infestations and treatments.
These problems were addressed in the final recommendations.

May 5 - Sept 20- Surveys of insect pests in The Tower

Purpose and procedures.
Three surveys were undertaken, a continuous survey from May 5 - July 15 and two

single day surveys between August 12 - 19, and September 16 - 20.

All insects were collected from window sills in the tower, tentatively identified and their location recorded using the floor plans. These surveys were undertaken by staff in the individual collection care areas. The purpose of these surveys was to: assess the insect population (location;fluctuation; size; and source) and determine methods of eradication; test the survey forms; establish awareness of responsibility and cooperation with the staff;

A 2.2 Data and Interpretation of Results of May 5-Sept 20 Surveys Results.

The insects were identified (Table 1)
Megatoma vespula L. (carpet beetle)
Anthrenus verbasci L. (carpet beetle)
Tineola bisselliella Hummel (webbing clothesmoth)
Tinea pellionella L. (case making clothes moth)
Musca domesticius L. (house fly)
Stegobium paniceum L. (biscuit beetle)
Others include: ladybird beetles; large outdoor moths; fungus gnats; or other or other insects which are not potential pests but may be indicator species.

M. vespula L. (carpet beetle), A. verbasci L. (varied carpet beetle, T. bisselliella Hummel (webbing clothes moth), T. pellionella L. (case making clothes moth) are common household insect pests which have the potential of destroying proteinaceous artifact or research material. S. paniceum L. (biscuit beetle) is also a common household pest. It normally utilizes carbohydrate materials, but is also a threat to starchy plant materials. Thus these insect found in this survey pose a threat to the museum collections.

The raw data was tabulated to show the population and species distribution by floor, window and floor/window. Only one example of each type of interpretive chart of the data will be presented to illustrate the methodology. The distribution, concentration and fluctuation of the insects was analysed environmental indicators, and insect relationships was studied.

Distribution by Floors

	1	2	2M	3	3M	4	4M	5	5M	6	6M	7	7M
1st	17	6	9	19	12	6	17	41	27	16	8	2	50
2nd	4	0	2	3	4	27	0	13	4	18	33	57	7
3rd	3	4	1	3	2	4	3	3	3	0	3	20	14
TOTALS	24	10	12	25	18	37	20	57	34	34	44	79	71
													465

Table 2. shows the total number of insects by floors on the three surveys.
The three surveys are designated as follows:
1st - a continuous survey from May 5 - July 15;
2nd - a one day survey done between Aug 12. - 19;
3rd - a one day survey done during the period of Sept. 15 - 20.

From Table 2. showing the total number of insect collected on the individual floors the following is observed: Main floors have more insects than mezzanine; there are progressively higher numbers of insects the higher the floor; 2nd and 2M have the least number of insects, which reflects their excellent maintenance program and no inaccessable floor areas; the initial survey had significantly higher numbers of insects because it was an accumulation over a longer period of time than the last two.

	VCB	MCB	FLY	OTHERS	TOTALS
1	8	1	10	5	24
2	0	4	1	5	10
2M	5	2	1	4	12
3	19	2	1	3	25
3M	4	1	3	10	18
4	4	2	27	3	37
4M	4	0	14	2	20
5	3	19	7	28	57
5M	11	3	8	10	34
6	21	0	10	4	34
6M	34	0	9	1	44
7	14	1	3	61	79
7m	16	0	51	4	71
Totals	143	35	147	140	465

Table 3. Total numbers of the individual species collected on each floor of the Curatorial Tower from the three surveys: Anthrenus verbasci L. (varied carpet beetle) - VCB; Megatoma vespula L. (carpet beetle) - MCB; and Musca donesticius L. (house fly) and Others (gnats etc.)
Table 3 shows the tabulation of the number of individual species on each floor. The large number of VCB on 3 & 6M are probably related to the infestations that were on these floors. It is impossible to come to conclusions because of the prior irregular maintenance of the window sills, it may be that 6M has not been cleaned over a longer period than others. One of the advantages gained from these surveys is that all insects will be removed and a zero point

established for future surveys. The population size of Megatoma beetle is small. A survey of the area did not reveal an active infestations, but an open vent to the outside was located on a nearby window.

The largest number of flies were found on 7M, this indicates a building infested with VCB larvae.

The Other insects were mainly fungus gnats and the large concentrations were adjacent to areas where there were potted plants. They are environmental indicator species.

Distribution of species by window

	VCB	MCB	FLY	OTHERS	TOTALS
1	1	3	1	9	14
2	6	2	4	7	19
3	0	2	1	1	04
4	5	2	6	2	15
5	19	2	3	59*	83*
6	15	0	5	0	20
7	5	0	4	0	09
8	3	3	6	1	13
9	8	0	11	5	24
10	17	1	4	7	29
11	1	1	10	4	16
12	7	1	5	2	15
13	1	3	2	6	12
14	0	0	3	0	03
15	2	1	5	1	09
16	3	2	6	0	11
17	1	0	6	2	09
18	1	1	3	2	07
19	5	0	9	2	16
20	7	0	5	3	15
21	2	1	5	0	08
22	10	1	5	5	21
23	8	0	1	2	11
24	2	3	8	2	15
25	5	2	16	6	29
26	4	1	4	7	16
27	0	3	3	1	07
28	2	0	6	4	12
Totals	140+3	35	147	140	462(+3)**
%	30.75%	7.52%	31.61%	30.10%	

Table 4. Total number of insects form the three surveys: Anthrenus verbasci L (varied carpet beetle)-VCB; Megatoma vespula L. (carpet beetle)-MCB; and Musca domesticius L. (house fly) and others (gnats etc.) collected at the specific windows (1-5 east facing windows 9-19 south facing windows, 20 - 28 west facing windows, 20-28 west facing windows) totalled from all floors for the three surveys (* = approx., ** = not assigned to a window).

Table 4. tabulates the individual insect species according to window. It shows the following: there is no distinctive distribution according to window; the size of the VCB population is approximately the same size as the fly population; there is a slight selection of south east and west windows for total insects; the highest concentration of flies is on the west windows; the varied carpet beetle according to this information show a selection towards the south east windows; Megatoma beetle and others show a diffuse distribution.

Distribution of insect species by window and floor

	1	2	2M	3	3M	4	4M	5	5M	6	6M	7	7M	TTL
1	1													1
2				1				1	1	1				4
3														0
4				1				1			1			3
5				6						3	8	1		18
6				5						4	5			14
7				1						3		1		5
8				1										1
9							1		2	2	1			6
10	1	1			1					1	7	4	2	17
11								1						1
12				1					2	1	1		1	6
13														0
14														0
15								1		2			1	4
16														0
17	1													1
18														0
19										1				1
20	2									1	4			7
21												1		1
22	2				1		1		2	1			1	8

	1	2	2M	3	3M	4	4M	5	5M	6	6M	7	7M	TTL
23					1	2			1	1			4	9
24	1				1		1							3
25							2		1				1	4
26			1	1		1							2	5
27														0
28						1			1			2		4
Totals	8	1	1	17	4	4	5	4	10	21	27	9	12	

Table 5. distribution of Anthrenus verbasci L. (varied carpet beetle)- VCB; on each floor window by window (1-5 east facing windows 9 - 19 south facing windows, 20 - 28 west facing windows).

Only one table (Table 5.) showing the distribution of insect species by window and floor is presented. The population of the A verbasci L. (varied carpet beetle) is presented. This two dimensional chart shows two distinct populations which are located in the areas where active infestations had been located. The one on 3rd floor (windows 4 - 7) is very localized and the one 6/6M (windows 5-8) is more diffuse, which suggests that it is a population that may have been active for a longer time and has spread out. These two populations are located on the south east windows. The diffuse distribution on nearly all floors by the south west windows suggest a building problem. This type of representation of the data gives an excellent insight into the insect populations.

Fluctuations and number of species over time

It was impossible to tally all the information chronologically because the initial count for the first survey varied from May 5 - July 14. The 5 and 5M floors were surveyed methodically over this period and showed minimal fluctuation of insect species. The environment in which the insects were found was constant, thus any fluctuation in the numbers and species of insects suggests an outdoor variable environmental influence which would support the premise that the insects are coming into the building from the outside with the exception of the isolated infestations. The Megatoma beetle showed an occurrence on 5th floor May 22, a peak of the population on June 6th and decline by June 18th, the overall total was only 10 insects. Two more were found one month (July) later, and five more the following month (Aug) and none the next month (Sept.). There appears to be an increase in gnats/others at the same time as the Megatoma appearance and increase occurred. Of the other insects there appears to be no signigicant fluctuation in numbers. It is difficult to work with such small numbers, but tendencies are probably legitimate.

2.3 Significance of the Insect Species and Distribution

i. potential problem insects;

Both the varied carpet beetle and the Megatoma carpet beetle could cause artifact materials. The varied carpet beetle has been found in infestations of skeletal material associated with horn in Vertebrate Zoology and Archaeology.

The obvious danger of the presence of these insects is the possible introduction into vulnerable materials in the collection. This could come about by dusting the window sills and redistributing the insects to the floor where they could be picked up on a dust mop and carried into the collection areas. Also it is possible that objects placed on sills could harbour the beetle adults or larvae, and the relocation of these objects near to collection could further distribute the insects.

ii. Varied carpet beetle and fly interaction-natural population ecology of Museum insects.

Examination of the house flies showed that a large majority were eaten by larvae of both the Varied Carpet Beetle and the Megatoma beetle. It is important to notice that the size of the random population of the VCB is close to that of the fly. This is an important observation, it shows the natural inter-relationship ofthese flies and the beetles. Because of the small number of insects present in a more or less random distribution, the populations of insects could be considered as natural populations within the tower exhibiting natural population ecology.

iii. indicator species which indicate building problems;

The presence of flies indicate that some how insects are getting into the supposed sealed environment of the tower.

iv. source of the insects according to natural habitat or building problem.

The source of the large numbers of VCB in specific areas came from local infestations in the collections.

The insects in the overall diffuse pattern suggest that they originate from outside the building or from internal building shell structure.

The Megatoma beetle occurence and fluctuation in a constant environment supports the premise that the insects come from outside.

There is no evidence that the insects come in with the air supply. There are two air filters the finest down to the micron level, which should not allow such large material as insects in. Tests with cotton cheese cloth placed over the air vents did not capture flies over a period of 1 month, and at the same time 10+ flies have appeared on the windows. It is also important to note that the flies are often found alive, there is no place for pupation of flies in the Museum environment, they must come in alive from outside.

The large numbers of "others" which include, large outdoor moths, fungus gnats, or other insects which are not potential pests suggest a local source i.e. flowers or potted flowers or local building problem.

2.4 Assessment of Survey Procedures

Assessment of procedures for its applicability for future surveys and monitoring procedures.

The first survey was undertaken over a period of approximatly two months. This proved to have both negative and positive results.
Negative: the coordinator was not informed soon enough after changes in insect species or concentrations; the flies that were collected may have appeared dead but many harboured live larvae which should have been immediately assessed; the long period of time included many holidays and a continious survey was not possible; the initial count of insects was done at different times and puts the data out of wack.
Positive: the continuous survey showed changes in the species and numbers of insects; the form was successful in respect to ease of recording accurately and interpretation of results.

The following two surveys were done on a single day. The insects collected represented the accumulation of approximatly one month, thus the fluctuation of species and increase in numbers over this period was masked. For future surveys it has been decided to do a continuous biweekly survey.

3. Survey of Ellery Street warehouse

The large size of the warehouse (approx. 20,000 sq') and complexity of the storage of artifacts on pallets placed on high shelving made the inspection of the artifacts impossible. It was decided to collect cobwebs and dust and examine these for evidence of insects. Even though the maintenance of the floor was good, there were still fragments of cobwebs adjacent to base frame work of the shelving and in cracks of the cement. Exoskeletons of insects could be easily identified. A floor plan showing the location of the sample is necessary. This method proved adequate and fortuitously allowed us to zero into a beetle infestation in a herbal collection.

For continued success of this method of monitoring, it is essential that after collection of the samples that the floor areas sampled be vacuumed clean so as to have zero reference point for the next survey.

4. Survey of Curatorial Tower stairwells, Oct. 21 - 23, 1986

The unheated stairwells at the N.E. and N. W. end of the Curatorial Tower have windows on the east and west side of each stairwell. Every other window is set at floor level and the alternate at waist level. Dust had accumulated in the floor level window where the caulking was absent or incomplete. Dust samples were removed and examined under the dissecting microscope. After examination they were then frozen for 48 hours as a precaution against live insects. Analysis shows very few insect remains, two varied carpet beetle, 9 Megatoma beetle, 11 webbing clothes moth, 30 flies, and 16 mosquitoes, these insect species were also found in the Tower. In addition remnants of one Larder beetle was found in the Pent house on 8th floor, where a dermestid colony was housed several years back. The only living insects was three flies. The purpose of the analysis was to determine if there was a significant number of insects, which would indicate a source or a problem.

The Tower stairwells have open venting at the main floor and an open vent on the ceiling of the top floor. The presence of mosquitoes indicate that these insect are coming through these vents. Flies may also come in this way.
It was reported in April that clothes moths were seen in the stairwell between 3 and 3M. and some were captured in the front office on the 3rd floor (north west corner adjacent to the stairwell.). The presence of insect remains and a large number of larval moults in the west stairwell windows adjacent to 3 and 3M, suggest an active infestation at one time. It would be a restricted colony but is obviously the source of the moths seen in April.

The analysis of the dust was an adequate method of survey.

Overall Conclusions

The methodology presented proved successful in accomplishing the insect pest surveys which was undertaken to determine the presence or extent of an insect

problem in the Museum buildings and define the procedures for control and eradication. There is not a major insect problem in the Museum buildings. The active insect infestations have been eradicated. The source of the diffus populations of insects has not been definitively shown, but building problems are suspected.

RESUME

La désinfection à l'oxyde d'éthylène ,de textiles préalablement traités au pentachlorophénate de sodium, a conduit à une réaction exothermique entre le pentachlorophénate et l'oxyde d'éthylène. Cette réaction a probablement été initiée par une autre réaction également exothermique entre l'oxyde d'éthylène et les mordants métalliques de teinture d'une robe de soie. Elle semble également avoir été réactivée au cours du rinçage à l'air après la désinfection.

Elle aurait probablement pu être considérablement réduite:

-si la concentration en oxyde d'éthylène avait été de l'ordre de 125g par m3

-si l'atmosphère de traitement et de rinçage avait été un gaz inerte

-si les objets n'avaient pas été confinés dans les emballages.

Photo 1

L'OXYDE D'ETHYLENE. UTILISATION ET LIMITES . ACTIONS SECONDAIRES AVEC UN RESIDU DE TRAITEMENT ANTERIEUR.

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Les matériaux organiques, bois, textile, papier, cuir, qui entrent pour une part importante dans la constitution des collections sont particulièrement sensibles à l'attaque des insectes et des moisissures.

L'oxyde d'éthylène,désinfectant gazeux donc pénétrant, polyvalent car à la fois insecticide et fongicide, présente de grands avantages. Néanmoins, des études récentes effectuées à la suite d'un accident survenu lors d'une désinfection de masse, ont mis en lumière des limites à l'utilisation de ce produit.

1. Intérêt de l'oxyde d'éthylène

L'oxyde d'éthylène est parmi les gaz désinfectants un de ceux qui possède la plus petite molécule. Son pouvoir pénétrant est donc important, surtout si le vide a été fait préalablement à la désinfection proprement dite. Il assure une efficacité certaine au traitement des larves d'insectes situées à l'intérieur des matériaux compacts comme le bois.

L'oxyde d'éthylène est à la fois insecticide, fongicide et bactéricide. Cette triple action est très intéressante, la plupart des objets appelant au minimum un traitement insecticide et fongicide. De plus certaines moisissures qui ont poussé sur un substrat glycériné font preuve d'une résistance particulière vis-à-vis des désinfectants non gazeux comme les sels d'ammonium quaternaires(1) les antibiotiques(2), les phénols(3). Dans ces circonstances, seul l'oxyde d'éthylène est efficace. Ce phénomène a été également constaté au Musée des arts et traditions populaires sur une collection de cuirs anciennement assouplis à la glycérine. (Ceci pose par ailleurs l'utilisation de la glycérine, souvent recommandée comme plastifiant des colles cellulosiques, assouplissant du cuir, de la vannerie ... et qui, par sa forte hygroscopicité, favorise le développement des moisissures)

2. Accident survenu au cours d'une désinfection de textiles

Une expérience malheureuse a permis au Musée des arts et traditions populaires de constater certaines limites à l'utilisation de ce gaz.

2.1. Circonstances de l'accident.

Dans le courant de l'hiver 1977-1978, une panne de climatisation, jointe à des infiltrations d'eau, provoque pendant trois à quatre mois, dans les réserves situées au troisième sous-sol du musée, une humidité relative importante de l'ordre de 70 à 80 %. Il s'en suit une prolifération considérable d'insectes et de moisissures. Le laboratoire de restauration prend alors l'initiative d'une intervention en deux temps :

1) à court terme, disséminer dans les endroits les plus touchés les insecticides et fongicides disponibles. La protection fongicide consistait à imprégner des feuilles de papier de soie avec du pentachlorophénate de sodium ou de l'orthophénylphénolate de sodium dissouts dans l'alcool et, les feuilles étant sèches, d'en entourer les objets atteints pour faire barrière à la dessimination des spores.

2) à moyen terme, trouver un service apte à assumer la désinfection insecticide et fongicide de plusieurs dizaines de m3 de collections. L'oxyde d'éthylène, insecticide et fongicide, évitait deux traitements successifs et permettait la désinfection à l'intérieur des conditionnements, ce qui est appréciable pour un traitement de masse exécuté par un service extérieur au musée. Le seul service qui pouvait prendre en charge cette opération était le service de désinfection de la ville de Paris qui avait déjà travaillé pour un certain nombre de musées. Le traitement était effectué dans un mélange de 50 % d'oxyde d'éthylène dans l'air, sous pression légèrement inférieure à la pression atmosphérique pour éviter les risques d'explosion.

En décembre 1979, une première opération était engagée. Elle concernait une soixantaine d'emballages en carton d'environ 1/2 m3 chacun, répartis dans deux enceintes et contenant essentiellement des costumes ethnographiques. En ouvrant la porte pour sortir les objets de l'enceinte après les deux rinçages habituels, le technicien perçoit une odeur qu'il prend pour une odeur d'oxyde d'éthylène et il commande un rinçage supplémentaire. C'est après cette opération qu'il aperçoit une fumée sans flammes qui sort d'un emballage.

Un seul emballage sur soixante a été touché. La brûlure qui semble s'apparenter à une combustion lente s'est manifestée au centre du carton et s'est propagée en diminuant d'intensité, vers les parois, comme le témoigne l'état des objets touchés dont on a pu reconstituer la stratigraphie dans l'emballage grâce aux listes établies au cours du déménagement (photos 1 à 5). Il n'y avait dans cet emballage que de la laine, de la soie, du coton, et 3 ou 4 agrafes métalliques légèrement rouillées. Les deux objets les plus touchés étaient deux robes noires, contigües, l'une en soie, l'autre en laine. Sur les photos faites après l'accident des robes pliées comme dans l'emballage, puis des robes dépliées, on constate que la brûlure est rectangulaire et qu'elle s'est propagée verticalement à travers les diverses épaisseurs de textiles. Pour les robes les plus touchées (photo 1), cette brûlure a des dimensions comparables à celles des feuilles de papier de soie que l'on avait imprégnées de fongicide en 1978 et dont certaines avaient été introduites à l'intérieur des costumes très atteints. D'où l'hypothèse probable qu'une de ces feuilles aurait été laissée par inadvertance lors de l'emballage pour la désinfection, opération qui s'est effectuée dans la précipitation.

Photo 2 Robe pliée.

2.2. Hypothèses sur les causes de l'accident

Il est à noter que sur 60 emballages, un seulement a été touché, que la brûlure semble avoir été activée au rinçage, qu'elle a une forme rectangulaire bien déterminée qui semble s'être propagée en diminuant d'intensité dans la masse de textile. Ces différentes remarques conduisent à éliminer l'hypothèse selon laquelle les dégâts seraient imputables à la forte concentration d'oxyde d'éthylène et au mélange avec l'air. Par contre, l'image d'un fer à repasser oublié sur une pile de linge s'impose et nous conduit à la question : quelle surface a chauffé et pourquoi ? Une enquête menée auprès de spécialistes de la désinfection dans les musées, jointe à un dépouillement de la bibliographie sur l'utilisation de l'oxyde d'éthylène,révèle un certain nombre d'incidents plus ou moins graves :

- des pigments de bleu de prusse prennent feu lors d'une désinfection de cosmétiques, après l'évacuation de l'oxyde d'éthylène, à l'admission de l'air du premier rinçage (6).

- R.M. Organ, dans une lettre qu'il m'adresse le 22 janvier 1980(7) parle de réactions possibles sur les salissures des vêtements, résidus de transpiration ou de nourriture.

- Mme Fabre,représentant le service de désinfection de la ville de Paris,lors d'une réunion sur les causes de l'accident le 23 janvier 1980,évoque un phénomène du même type, survenu en 1968 au cours de la désinfection de passementeries où une inflammation s'est manifestée à l'ouverture des portes, après deux rinçages à l'air.

- M. Morisseau, directeur de la maison Mallet, constructeur français des enceintes de désinfection, cite au cours de la même réunion, le cas de la désinfection d'un tableau d'art moderne qui présentait un développement important de moisissures et dont le vernis semble avoir fondu pendant la désinfection, ce qui amène à nouveau à penser à un échauffement.

Ceci nous paraît suffisant pour ne pas mettre la responsabimité de l'accident sur les seuls risques dus au mélange oxyde/air, et à nous interroger sur l'apparition d'une réaction exothermique, ses causes, les conditions de son développement. Une étude dans ce sens est confiée au Centre de Recherche sur la Chimie des Combustions à Hautes Températures (C.R.C.C.H.T.), sous la direction de M. Delbourgo, puis de M. Méllottée. Les résultats obtenus par M. Méllottée au C.R.C.C.H.T. (8) et ceux de M. Chaigneau (9) à la Faculté de Pharmacie de Paris permettent d'envisager un scénario probable pour l'incident de décembre 1979.

Photo 3 La même robe, dépliée.

3. Extraits du rapport de M. Méllottée

Le scénario de l'accident exclut toute réaction d'inflammation ou de combustion de l'oxyde d'éthylène lui-même ou des mélanges entre l'oxyde d'éthylène et l'air, réaction qui se serait manifestée par un développement au sein de la phase gazeuse et non pas dans les tissus soumis au traitement de désinfection.
La cause de l'incident est dûe selon toute probabilité à la réactivité très élevée de la slie d'une des robes avec l'atmosphère contenant de l'oxyde d'éthylène. Ce n'est d'ailleurs pas la soie en général qui pose problème puisque l'analyse thermodifférentielle (ATD) de soie brut a montré une certaine inertie de celle-ci à l'oxyde d'éthylène. C'est plutôt la soie de la robe traitée qui a conduit à l'incident à cause des produits ayant servi à modifier ce tissu (charges, apprêts, colorants, teintures ...) (Fig.1)

Photo 4 Robe pliée

Photo 5 La même robe dé-
pliée

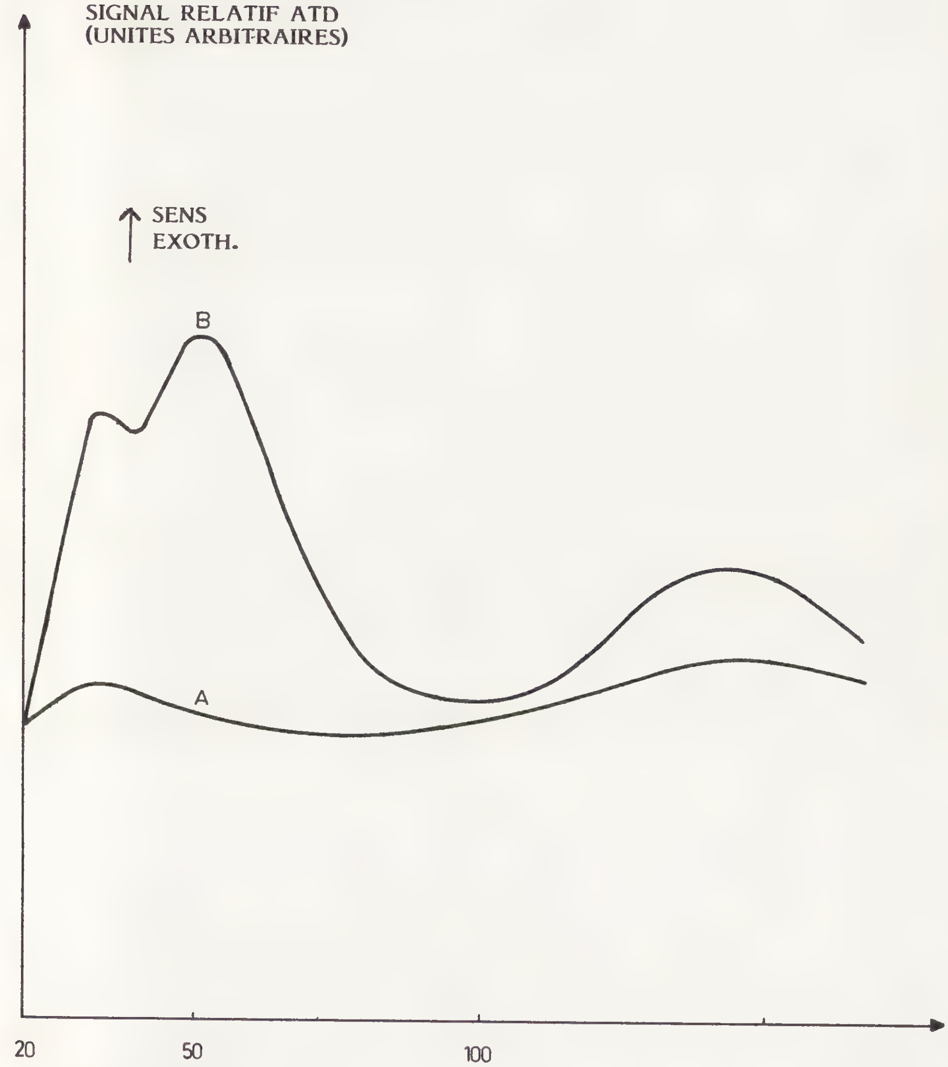

FIGURE 1 : SIGNAL RELATIF ATD DE LA SOIE
(SIGNAL SOUS OXYDE D'ETHYLENE MOINS
[Réf (8)] SIGNAL SOUS AIR)

A OXYDE D'ETHYLENE 20 % - AIR 80 %
B OXYDE D'ETHYLENE 100 %

La réactivité élevée de cette soie a été mise en évidence tant par les expériences en ATD que par les essais de chimisorption de M. Chaigneau (9). Elle est à rapprocher des réactivités mentionnées dans la littérature de l'oxyde d'éthylène avec différents composés chimiques (oxyde de fer, sels d'étain) dont on sait par des analyses menées à l'Institut Textile de France et au Service Central d'Analyses du C.N.R.S., que les teneurs étaient loin d'être négligeables (5,87 % de fer dans la chaîne et 4,2 % dans la trame). Il est clair que ces composés sont présents sous forme très divisée sur la soie, ce qui facilite leur réaction avec l'oxyde d'éthylène. Le doute subsiste sur le mode de réaction de l'oxyde d'éthylène avec ces substances. S'agit-il d'une polymérisation (exothermique) de l'oxyde d'éthylène ou d'une réaction de décomposition (exothermique elle aussi) ? Mais quoi qu'il en soit, l'effet exothermique de ces réactions contribue à élever la température de la soie, comme l'ont montré les expériences en ATD et des essais menés dans une petite enceinte de désinfection (fig.2)

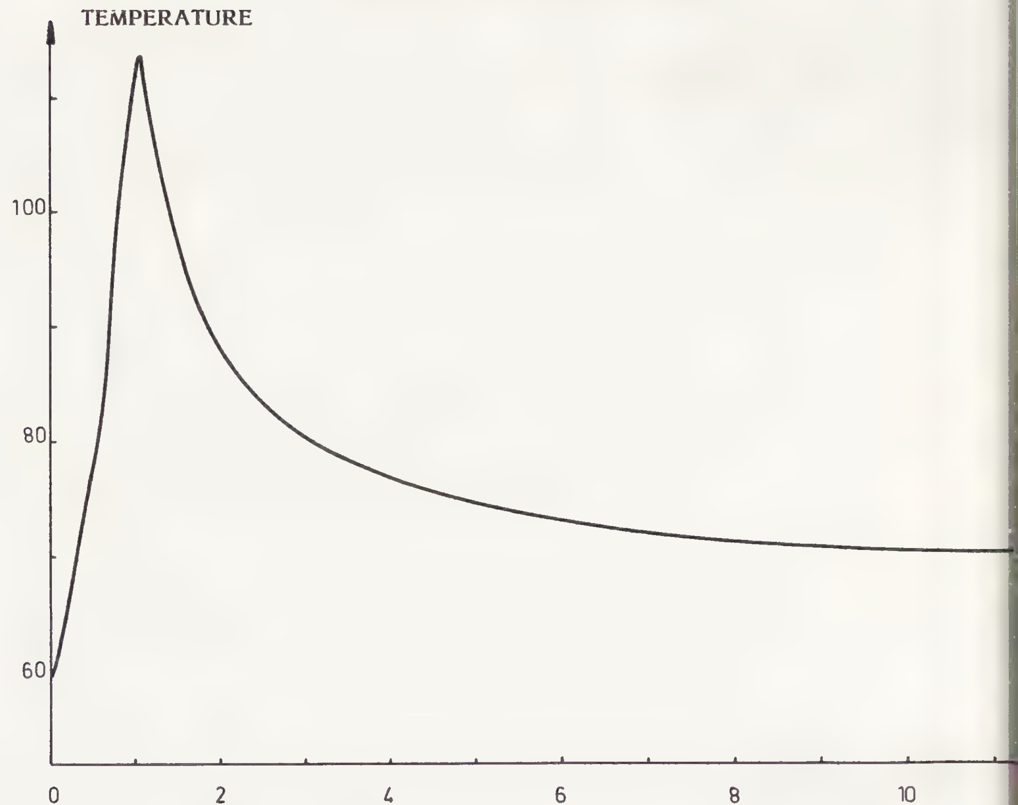

FIGURE 2 : EVOLUTIONDE L'EFFET THERMIQUE DANS L'ENCEINTE LORS D'UN TRAITEMENTPAR OXYDE D'ETHYLENE DE BOITE[S] CONTENANT LA SOIE DE LA ROBE ATTEINTE

[Réf (8)]

Ni le papier, ni l'orthophénylphénolate de sodium ne semblent avoi[r] eu un rôle dans les incidents étudiés (fig.3)

Par contre, le pentachlorophénate de sodium paraît avoir été un élément actif. En effet, l'ATD a révélé une réactivité d'autant plus importante que le taux d'oxyde d'éthylène dans le mélange gazeux est élevé (fig.4).Le processus d'ATD suppose une élévation progressive volontaire de la température. Mais dans le cas de la soie, l'élévation de température due aux réactions entre l'oxyde d'éthylène et la soie suffit à provoquer la réaction entre ce même gaz et le pentachlorophénate de sodium.Il est probable que ces deux cuases simultanées d'élévation de température ont suffit pour atteindre les températures nécessaires pour provoquer la carbonisation du tissu. En effet,il est remarquable de constater que la soie de la robe subit une dégradation très rapide dès les basses températures. Son analyse thermogravimétrique sous air ou sous azote a montré que le tissu perd en effet de l'humidité dès 40 ou 50 ° mais ne cesse ensuite de se dégrader, et cela avec des vitesses élevées à partir de 240 ou 250 °. Il est à noter aussi que la nature du gaz diluant importe peu puisque vers 350° les processus de dégradation sont identiques. Il reste à se demander, compte tenu des remarques faites au cours de l'incident de 1979, quelle peut être l'influence

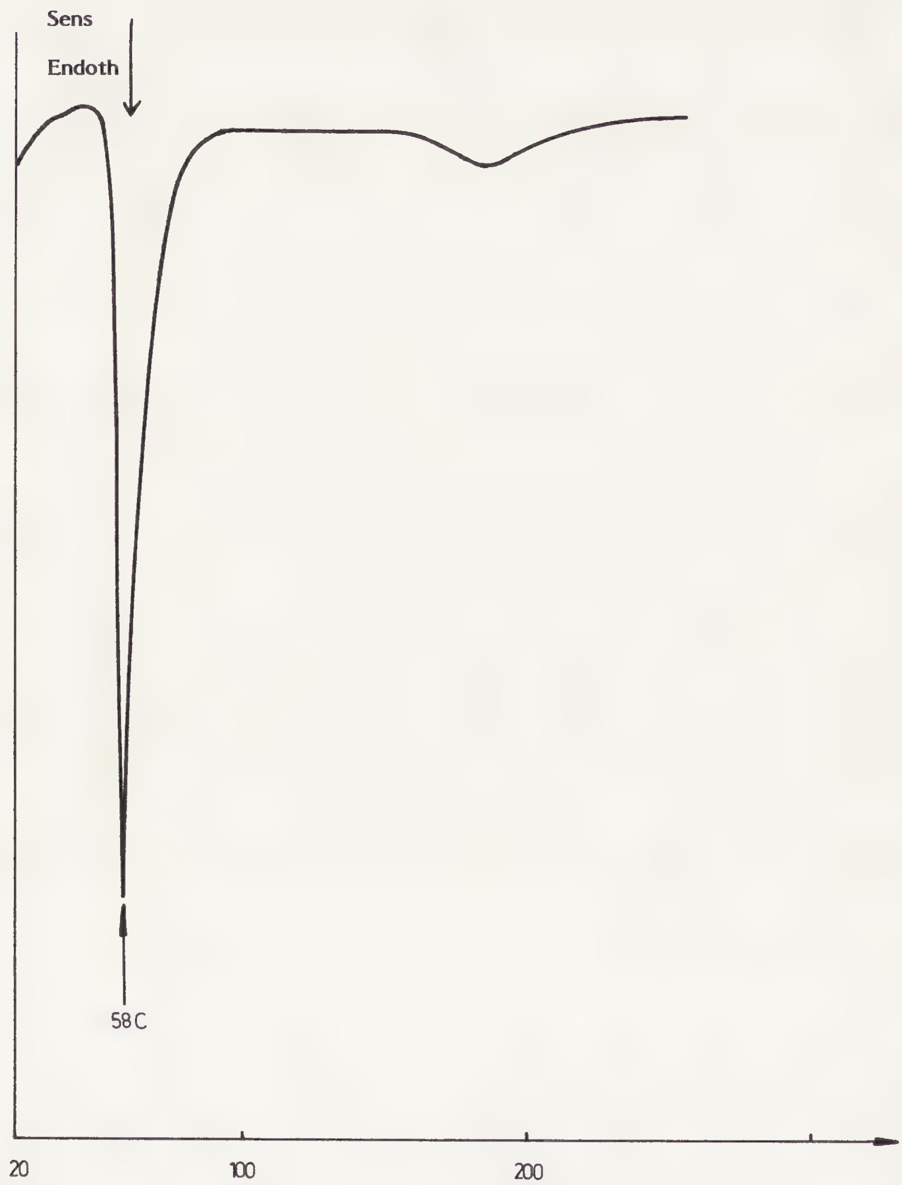

FIGURE 3 : SIGNAL ATO DE L'ORTHOPHENYLPHENOL
[Réf (8)]

de l'ouverture de la porte de l'enceinte (et donc de l'entrée d'air) sur la dégradation finale observée. L'hypothèse la plus vraisembable consiste à penser que les processus décrits plus haut ont porté le tissu localement à une température de l'ordre de 300 ° : l'entrée d'air, c'est-à-dire l'élévation du taux d'oxygène a pu très rapidement conduire à une réaction d'oxydation du tissu, l'élévation de température résultante entraînant la dégradation rapide du tissu ainsi que celle du pentachlorophénate de sodium.
L'accident de décembre 1979 serait dû à une conjonction "remarquable" de faits ayant concouru à la dégradation observée :
- la robe de soie était particulièrement peu stable au point de vue thermique ;
- les additifs de la soie étaient très réactifs et de façon fortement exothermique avec l'oxyde d'éthylène ;
- le pentachlorophénate de sodium est lui-même très réactif et également de façon exothermique. (ce dernier effet pouvait être minimisé en diminuant le taux d'oxyde d'éthylène)
Ces conséquences pouvaient être réduites en utilisant des gaz inertes comme l'azote ou les fréons. Encore aurait-il fallu que les objets ne soient pas confinés pour que la chaleur dégagée par une réaction issue de l'un d'eux puisse se disperser dans le gaz inerte et non dans la masse de l'objet voisin. Dans le cas de l'accident survenu en 1979, on peut craindre que le gaz inerte n'ait pu jouer convenablement son rôle, les textiles étant confinés dans leur emballage.

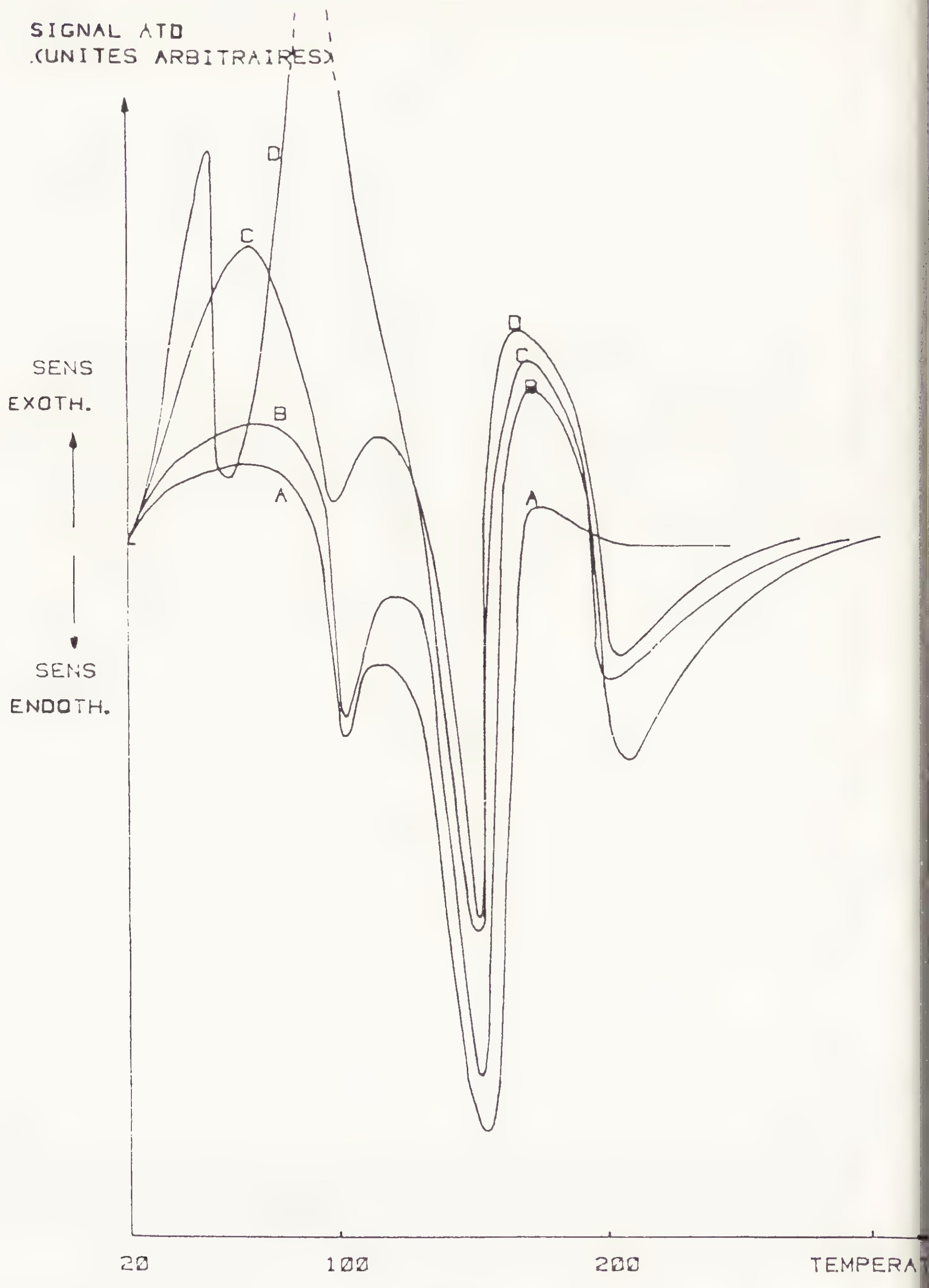

FIGURE 4 : EVOLUTION DU SIGNAL ATD DU PENTACHLORO-PHENATE DE SODIUM SELON LE GAZ DE TRAITEMENT

A AIR 100 %
B AIR 80 % - OXYDE D'ETHYLENE 20 %
C AIR 50 % - OXYDE D'ETHYLENE 50 %
D OXYDE D'ETHYLENE 100 %

[Réf (8)]

4. Conclusions

Les risques d'explosion de l'oxyde d'éthylène en mélange avec l'ai[r] étaient déjà en 1979 presque universellement contrés par son utilisation avec des gaz inertes. Par contre, on ne trouve pas à cette époque, dans la bibliographie qui nous concerne, de références à des études concernant des réactions secondaires entre l'oxyde d'éthylène et les oeuvres d'art.

L'étude menée par M. Méllottée a mis en évidence une cascade de réactions secondaires entre l'oxyde d'éthylène, les additifs du textile, un résidu de traitement antérieur. Ces réactions se sont produites avec dégagement de chaleur et ont causé sur les objets vieillis dont la résistance aux effets thermiques est considérablement amoindrie, des dégradations qui auraient pu ne pas se manifester sur des matériaux neufs.

La probabilité pour qu'un tel accident se reproduise n'est pas négligeable. En effet, le pentachlorophénate de sodium a été souvent conseillé comme agent préventif et curatif dans la lutte contre les moisissures. Il a été utilisé soit imprégné dans du papier de protection, soit pulvérisé sur les objets, soit au coeur même des matériaux comme additifs dans certains adhésifs. On sait qu'il s'hydrolyse à long terme en devenant acide. On sait par ailleurs que la réactivité de l'oxyde d'éthylène est importante avec de nombreuses fonctions chimiques : atomes de chlore réactifs, groupements OH,NH2,SH ... Ces réactions, généralement exothermiques, sont catalysées par des traces d'acide, de base ou des oxydes métalliqques (10). Il semblerait donc prudent de connaître les traitements antérieurs à tout passage à l'oxyde d'éthylène pour prendre les précautions nécessaires en cas de risques d'incompatibilité.

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UMMARY

Federal regulations in the United States were revised in the late 1960's because of growing concern of impact of pesticides on the environment and people. The U.S. National Park Service, through the Department of the Interior, developed an Integrated Pest Management Program that would require approval for use of pesticides and place an emphasis on exploring non-chemical methods to eliminate pest problems. This IPM program is explained and a listing of projects that have been reported through the formal approval process and that relate to museum collections are listed. A description of how the IPM program in one of the National Park Service's regions works with the museum personnel and their pest problems is included.

INTEGRATED PEST MANAGEMENT IN THE UNITED STATES NATIONAL PARK SERVICE

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In the United States, increased environmental concerns and awareness of the potential dangers of pesticides in the late 1960's led to the amending of existing and the creating of new U.S. federal regulations controlling the use of pesticides. The Federal Insecticide, Fungicide and Rodenticide Act of 1947 (FIFRA) regulated labelling of all pesticide products to insure that the products were effective and minimum safety precautions were included on the labels. The Federal Environmental Pesticide Control Act of 1972 (FEPCA or FIFRA as amended) expanded and revised the previous pesticide regulation by adding a requirement regulating the use of pesticides only when this use would not result in unreasonable risk to humans or the environment. FEPCA (or FIFRA as amended) was amended in 1975 and again in 1978 by passage of the Federal Pesticide Act which revised the product registration process by establishing the generic registration procedure.

Concern about the use of pesticides spread from primarily agricultural sources to major land management agencies dealing with natural resources and institutions concerned with the preservation of natural and cultural resources (such as museums and historic preservation groups). Pesticides had been frequently used as fumigants for museum collections and structures, many times without proper documentation as to what was done and not using proper application methods to insure that the application would be most effective. The impact of the pesticide on the resource, whether it was natural or cultural, was rarely considered.

The United States Department of the Interior was one of the major groups to become concerned about the level of pesticide use. The Department of the Interior contains some of the major public land management agencies, amongst these agencies is the National Park Service. The National Park Service is the major U.S. agency responsible for overseeing the preservation of natural and cultural resources. A pesticide use policy to comply with FIFRA as amended was developed by the U.S. Department of the Interior for inclusion in the Departmental Manual. This Departmental pesticide use policy was written to include the following provisions:

a. To allow use of pesticides only after full consideration of alternatives (chemical, biological, physical methods and no action). When it has been determined that a pesticide must be used, only the least hazardous material will be used.

b. To utilize pest management research, control, education and assistance programs to develop, support and adopt integrated pest management (IPM) strategies wherever practical.

c. To use only pesticides registered by the U.S. Environmental Protection Agency (EPA).

d. That the handling and use of restricted-use pesticides be conducted with caution and only by certified personnel.

e. To conduct monitoring before, during, and after any pesticide application in ecologically sensitive areas. Such monitoring should determine whether the pesticide achieved the desired effects and whether there are any significant, ananticipated effects.

Concurrent with the development of this Departmental policy, the U.S. National Park Service (NPS), decided to replace the existing pesticide use log system with a nationwide integrated pest management (IPM) system for its 337 parks. This IPM system is in use today. Originally developed in agricultural settings, integrated pest management as defined by the National Park Service is the selection, integration and implementation of pest control, using an information intensive program based on predicted economic, ecological and sociological consequences. A systems approach is used to reduce pest damage to tolerable levels through a variety of techniques, including natural predators (spiders, snakes, cats, etc.), genetically resistant hosts, environmental modifications (control of temperature and humidity, general housekeeping) and where necessary, chemical pesticides.

The IPM program established by the NPS is a decision-making process for determining if pest suppression is needed, when treatment is needed and where. The major components of IPM are:

Monitoring: Regular, written observations of pest populations or other indicators such as weather, signs of pest presence, natural enemies. Monitoring can be used to determine if a problem exists, if the potential for a problem exists, or if a treatment was successful.

Injury Levels: The amount of injury which causes intolerable ecomomic, aesthetic or resource damage. For museum collections, this level may be one pest.

Action levels: Time or period, based on monitoring data or other factors when action must be taken to prevent population from reaching levels that cause injury.

Treatments: Measures that are least disruptive to natural controls, least hazardous to human health, and least damaging to the environment or the resource.

Documentation: The written report of what pests were found, specific problem areas, what action was taken (including but not limited to chemical treatments) and recommendations for future use.

Evaluation: Continuous review of the IPM program to determine the effectiveness of monitoring, thresholds, and treatments.

The present IPM program for the NPS is organized with a centralized IPM Coordinator under the Biological Resources Division in the NPS Washington, D.C. office (WASO). The WASO IPM Coordinator oversees a library of information on pests, pesticides, non-chemical treatment options and monitoring and the development of educational materials and workshops. This person is also responsible for the approval or disapproval of pesticide projects using the Pest Control Program Report (FORM 10-21A).

Each of the ten NPS Regional Offices has a Regional IPM Coordinator, usually a staff person with a natural resources background. Each park area also has a IPM Coordinator. The Park IPM Coordinator is the person who identifies the pest problem and then works through the Regional IPM Coordinator to the WASO IPM Coordinator for possible non-chemical solutions or written official approval to use pesticides.

Information and educational materials are provided from the WASO IPM Coordinator through the Regional IPM Coordinator to the Park Coordinators. The WASO IPM Coordinator has produced a series of IPM Information Packages on a variety of pests. The Information Package includes a pest decision tree (see Fig. 2), pest biology and ecology, pest management and a bibliography. IPM workshops are given annually, both through the central WASO office and regional offices, on the general IPM program and on specific resource applications such as museum collections, structures, and gardens.

The Pest Control Program Report (FORM 10-21A, Fig. 3) is used by the parks to obtain approval to use pesticides for specific projects. This report is to be completed and submitted prior to undertaking a project involving pesticides and sent to the WASO office on an annual basis. Telephone approvals are possible if time is short, but the Park must send in a completed report within

Fig. 1

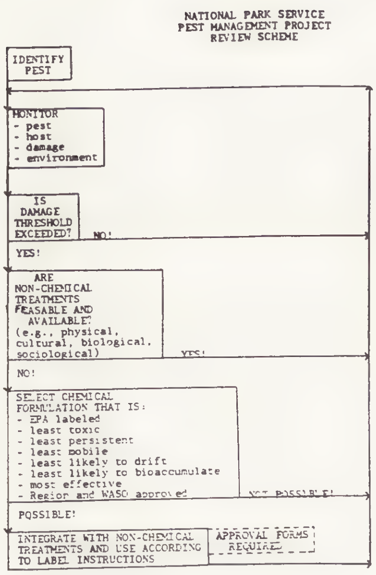

Fig. 2

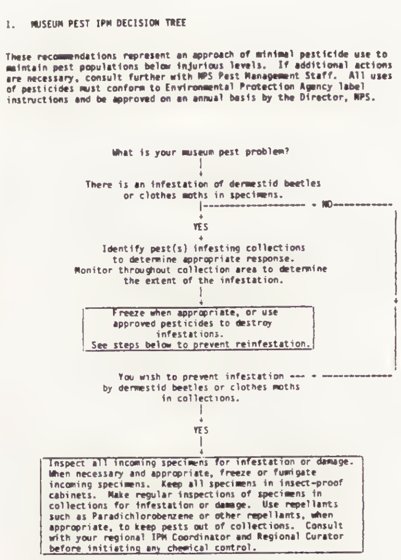

Fig. 3

FORM 10-21A
(REV. 11/83)

UNITED STATES DEPARTMENT OF INTERIOR
NATIONAL PARK SERVICE
PEST CONTROL PROGRAM REPORT

TARGET PEST:	REGION:	SIGNATURES OF APPROVAL
	YEAR:	PARK:________ DATE:____
PRODUCT NAME:	ORGANIZATION: PROJECT: (e.g., YELL-84-01)	REGION:________ DATE:____
EPA REG. #:	PURPOSE:	
ACTIVE INGREDIENT:	SEASON OR PERIOD OF APPLICATION:	
% or #/G (/) ACTIVE INGREDIENT:	AREAS TO BE AVOIDED:	
MIX OF PRODUCT WITH DILUENT:	AREAS TO BE TREATED WITH CAUTION:	
PRODUCT USAGE RATE:		
PRODUCT AMOUNT USED PER APPLICATION:	PRECAUTIONS:	
METHOD OF TREATMENT:	USE OF TRAINED OR CERTIFIED PERSONNEL:	
FORM APPLIED:	MONITORING:	
AREA OR UNITS TO BE TREATED:	PERSON TO CONTACT:	
NUMBER OF SITES:	OTHER REMARKS:	
DESCRIPTION OF SITES:		
NO. OF APPLICATIONS :		
AMT PRODUCT USED TOT:		

ten working days after notification of a project approval. Once the report is received by the WASO IPM Coordinator, approval or disapproval will be given within five working days. This report only documents chemical solutions to pest problems, not the non-chemical approaches that may have been tried initially.

The information on the submitted Pest Control Program Reports are entered in a computer in the WASO office. A list of the pests that have been reported each year is maintained as well as the types of pesticides and their active ingredients. A variety of information can be obtained from this nationwide data bank. The project information can be grouped by pest name, pesticide, geographical region, type of resource affected, and park.

Not all NPS pesticide projects have been submitted for approval through this centralized IPM program. Not all park personnel using pesticides are aware of this program or realize that formal approval to use pesticides is necessary. Cultural resource projects have not made use of this program in the past to the extent that the natural resource projects have. The IPM program was initiated through natural resource personnel and thus much of the training and project review concentrated on natural resources. However, in the past few years, the IPM Coordinators have made a concentrated effort to review and train cultural resource projects and personnel, in particular museum curators and historical architects, throughout the National Park Service.

A search was done of the existing Pest Control Program Reports on the WASO computer to see what types of information was currently available for the years 1985 and 1986. A list of projects grouped under the classifications "Museum" and "Structure" was obtained. The following listings are these projects, listed by type of pest. The listing for structures has been narrowed down to only include pests identified as being problems to museum collections. It should be noted that many more projects were found on the computer listing that named cockroaches and termites as the identified pest but it was unclear from the given information as to whether the projects involved structures that contained museum collections or the structures did not contain museum collections.

<u>MUSEUM PESTS</u>

Clothes moths - Great Smoky Mountains National Park (Tennessee), Museum Exhibit.
Pesticide - Paradichlorobenzene
Monitoring - Unknown

Casemaking Clothesmoths - Death Valley National Monument (California), Museum Storage.
Pesticide - Paradichlorobenzene
Monitoring - Yes

Webbing Clothesmoths - Death Valley National Monument (California), Museum Storage
Pesticide - Paradichlorobenzene
Monitoring - Yes

Dermestids - Great Smoky Mountains National Park (Tennessee), Museum Exhibit.
Pesticide - Paradichlorobenzene
Monitoring - Unknown

Grand Canyon National Park (Arizona), Museum Storage.
Pesticide - Paradichlorobenzene
Monitoring - Yes

Organ Pipe Cactus National Monument (Arizona), Museum Exhibit.
Pesticide - Drione (amorphous silica gel, piperonyl botoxide, pyrthrins, petro hydrocarbons)
Monitoring - Yes

Yosemite National Park (California), Museum Exhibit (Indian Culture Museum).
Pesticide - Vikane (sulfuryl fluoride), fumigation (1 treatment)
Monitoring - Unknown

Silverfish - George Washington's Birthplace National Monument (Virginia), Museum Storage
Pesticide - Boric Acid
Monitoring - Yes

Cape Cod National Seashore (Massachusetts), Museum Storage.
Pesticide - Paradichlorobenzene
Monitoring - Yes

<u>STRUCTURAL PESTS</u>

Booklice - Biscayne National Monument (Florida), Library.
Pesticide - Boric Acid
Monitoring - Yes

Beetles - Carl Sandburg National Historical Park (Tennessee), Museum Storage.
Pesticide - Vapona Strips (DDVP or no pest strips)
Monitoring - Unknown

Powderpost Beetles - Salem Maritime National Historical Park (Massachusetts), Historic Structure.
Pesticide - Dursban T.C.
Monitoring - Yes

Fredericksburg-Spotsylvania National Battlefield Park (Virginia), Historic Structure.
Pesticide - Dursban T.C.
Monitoring - Unknown

Hampton National Historical Site (Maryland), Historic Structure.
Pesticide - Dursban T.C.
Monitoring - Unknown

Cumberland Gap National Historical Park (Kentucky), Historic Structure.
Pesticide - Dursban T.C.

Dermestids - Cape Cod National Seashore (Massachusetts), Museum Storage.
Pesticide - Paradichlorobenzene
Monitoring - Yes

Nez Perce National Historical Park (Idaho), Museum Exhibits, Museum Storage
Pesticide - Drione, Amorphous Silica Gel
Monitoring - Yes

Western Archeological Conservation Center (Arizona), Museum Storage
Pesticide - Vapona Strips (DDVP or no pest strips)
Monitoring - Yes

Moths - Carl Sandburg National Historical Park (Tennessee), Museum Storage.
Pesticide - Vapona Strips (DDVP or no pest strips)
Monitoring - Unknown

Silverfish - Adams National Historical Park (Massachusetts), Historic Structure.
Pesticide - Boric Acid
Monitoring - Yes

Everglades National Park (Florida), Library.
Pesticide - Boric Acid
Monitoring - Unknown

Big Bend National Park (Texas), Library.
Pesticide - Boric Acid
Monitoring - Unknown

Federal Hall (New York), Historic Structure.
Pesticide - Boric Acid
Monitoring - Yes

Richmond National Battlefield Park (Virginia), Administrative Offices.
Pesticide - Boric Acid
Monitoring - Yes

Western Archeological Conservation Center (Arizona), Museum Storage
Pesticide - Vapona Strips (DDVP or no pest strips)

A discussion was held with one of the NPS conservators in the North Atlantic Regional Office (Boston) to determine what types of pest problems might be occurring in NPS museum collections that were not reported because pesticides were not used. The following list of pest problems were mentioned.

Acadia National Park (Maine) - Clothes Moths, Museum Storage
Treatment - Vacuuming, professional dry cleaning.
Silverfish, Museum Exhibits
Treatment - Boric Acid

Fire Island National Seashore (New York) - Termites and Powderpost Beetles, Museum exhibit and storage.
Treatment - Monitoring relative humidity to verify moisture problem before treatment with chemicals

Sagamore Hill National Historical Park (New York)- Dermestids, Museum Exhibits
Treatment - Vacuuming, good housekeeping

Morristown National Historical Park (New Jersey) - Clothes Moths, Museum Exhibit
Treatment - Vacuuming

Edison National Historical Park (New Jersey) - Silverfish, Library
Treatment - Boric Acid

Statue of Liberty National Monument (New York) - Norwegian Rats, Ellis Island
Treatment - Monitoring burrows, reidentifying pest as muskrats.

Vanderbilt Mansion National Historic Site (New York) - Dermestids, Museum Exhibit and Structure
Treatment - Vacuuming, cleaning, changing mats under carpeting prior to any chemical treatment.

In the North Atlantic Region, the Regional IPM Coordinator has worked closely with the conservators in the Regional Office and park curators to determine what types of pest problems exist that affect museum collections. She also discusses potential treatments to find out what treatments would not adversely affect museum collections. This region contains a large number of historic structures that are used to exhibit historic furnishings. Monitoring and treatments in these areas involve working with both the museum curators and historic architects. Emphasis has been placed on monitoring, both for pests and environmental conditions (temperature and relative humidity), to determine if a problem exists, to identify the problem, and to see if treatments have been effective. Preventive measures are recommended, such as good housekeeping (removal of dust, food, drinks, and smoking) and structural modifications (sealing cracks and crevices, repairs) to exclude pests where possible.

Conclusion

The U.S. National Park Service, through the Department of the Interior, has established policies and guidelines for use of pesticides and by establishing the NPS Integrated Pest Management Program, has created a means of regulating the use of pesticides so that an emphasis is placed on using non-chemical treatments instead of chemicals. The IPM program is being used by museum personnel within the National Park Service; this use is increasing as information on this program is spread to the individual parks through training and publications. This IPM program should result in more monitoring to identify problems and pests and less use of chemical products to eliminate pests. It has already resulted in better written documentation of the use of pesticides for NPS projects.

SUMMARY

Selection criteria for the fumigant and factors involved in the design of a fumigation facility are described, based on experience gained in setting up such a facility. The report takes in environmental concerns, personal health and safety, and object safety. It relates them to ways of arriving at a practical solution. These criteria were then applied to the design and construction of a facility at the Conservation Analytical Laboratory of the Smithsonian Institution

FUMIGATION, CHOICE OF FUMIGANT AND DESIGN OF FACILITY

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Introduction

Hector Monro in his "Manual of Fumigation for Insect Control", with a first edition in 1961, set out the principles of fumigation[1]. These principles:

Define that the agent must be in vapor or gaseous phase and not present as an aerosol. This molecular state gives good penetration on application and fast clearing after exposure.

Treat the problem of sorbtion where physicochemical bonding can cause retention beyond the period that would normally be expected.

Set out the effects of temperature and humidity.

Define the transient nature of fumigants, that there is no permanent pesticidal effect. This is an advantage for people who will later handle the object but is a disadvantage in that it does not prevent reinfestation.

Develop the valid approximation that it is the product of concentration and time that determines the fumigation effectiveness and that one of these factors can, to a certain extent, be traded off against the other.

The problem of selecting a fumigant is a difficult one. At least four, sometimes contradictory, points must be taken into account:

1. Operator safety during fumigation must be considered.

2. The safety of persons handling the object after fumigation is critical.

3. The disposal of the used fumigant from the fumigation chamber must be controlled.

4. Last but not least, any potential deleterious effects of the fumigant on the object must be taken into account.

At this time, knowledge of and sensitivity to each of these components has increased, restricting the choice of fumigant that can be used and making the design of a safe facility more complex. This paper describes some of the conservation and engineering factors to be considered and results from experience gained in the design and installation of a large fumigation facility at the Smithsonian Institution (SI).

Choice of Fumigant

Ethylene oxide (EtO) and methyl bromide (MeBr) were, up to several years ago, the preferred fumigants for chamber fumigation for museums. EtO was and indeed still is widely used industrially to sterilize medical instruments and agricultural products. It kills both insects and fungal spores.[2] and, to the eye, appeared not to damage objects. Initially the occupational safety regulations in the USA, for worker exposure to EtO, specified a TLV-TWA (Threshold Limit Value - Time Weighted Average) of 100 ppm for 8 hours per day, 5 days per week for the life of an individual. Local sewage authorities also allowed the effluent scrubber water, containing the spent EtO, to be discharged directly into the sewer.

Since that time, EtO has been identified as a carcinogen and the Occupational Health and Safety Administration (OSHA)[3] in the United States has progressively lowered the effective TLV-TWA to less that 1/2 ppm. The setting of a short term exposure limit (TLV-STEL) has been delayed but probably will be less than 5 ppm.

The less than 1/2 ppm limit is both difficult to measure and to achieve. In addition EtO tends to be strongly adsorbed in some materials[4], making their examination in a closed workspace a potential problem, for some weeks after fumigation. This is particularly evident for proteinaceous materials such as wool, furs, leather, etc. which strongly adsorb. The TLV-TWA over the work table can easily be exceeded, even with prolonged airing.

The use of EtO fumigation, whether carried out in-house or by an outside operator, requires well ventilated airing spaces with one-time-through air conditioning (no air recirculation) and frequent air changes to allow objects to divest themselves of residual fumigant. Certainly no connection with other air conditioning (HVAC) systems is permissible. OSHA regulations effectively require airing schedules for all loads to be proved to be adequate, a most

difficult situation with the wide range of objects normally fumigated in a museum.

More recently, local water authorities, fearful of upsetting the biodegradation processes in their sewage plants, are more stringent in allowing unusual substances to be added to sewage. Holding tanks, protected against access by people because of the toxic fumes, are feasible since EtO does eventually degrade to ethylene glycol[5] which is more benign to the sewage systems. Active chemical treatment has also been proposed. Depending on local regulations, venting the discharged EtO and its diluent gas with a diluting air stream through a stack is permitted, so long as computer modelling is carried out to ensure that dilution in adjacent accessible areas is less than 5 parts per billion.

In order to reduce the danger of EtO/Air mixture explosions, the EtO is supplied mixed with an inert chlorofluorocarbon (CFC). The usual formulation for is a 12% mixture with 88% dichlorodifluoromethane (Cl_2CF_2) or CFC-12. CFCs are also used as spray propellants for paints, cosmetics etc and as refrigerator working fluids.. The propellent use is being restricted internationally due to its alleged harmful effect on the ozone layer high in the atmosphere. Even a small 100 cubic foot chamber with this formulation will discharge around 35 pounds of CFC-12 per fumigation cycle. Formulations with carbon dioxide as the diluent are also used, but are more dilute and require higher chamber pressures.

A further important consideration is that the oxygen bond in EtO is an epoxide which is most reactive. There is increasing evidence that damage can occur to the object from exposure to EtO[6].

As a result of these factors, the SI and some other organizations[7] have decided not to use ethylene oxide on site. If, after due consideration has been given to its potential effect on the object, the fumigation were to be contracted out-of-house, then care must be taken of adsorbed EtO on the returned objects. To the writer's knowledge, no EtO fumigations have been carried out for the SI in the last two years, for this reason .

Because of the above, EtO which had been widely used, came under suspicion. Accordingly, a search for alternate fumigants was carried out and the whole problem of museum pests was more broadly reviewed. One study, carried out under contract to the Conservation Analytical Laboratory (CAL) of the SI by Mr. Keith Story, an entomologist working in the area of insect infestation, resulted in a book "Approaches to Pest Management in Museums" published by CAL[8].

From this study and in consultation with other authorities in the field[9] , we decided that sulfuryl fluoride (SF) best fitted SI requirements. "Vikane" brand SF is manufactured by the Dow Chemical Company and well described in their fumigation manual[10]. The other major possible fumigant, methyl bromide, CH3Br (MeBr), also manufactured by Dow, was eliminated on the basis of data presented in their manual and as the result of other private communications. Since MeBr is one of the lower homologues of a halogenated hydrocarbon, it has a high potential for softening resins and varnishes. Other Dow product literature specifically warns against its use on sulfur-containing compounds which include wool, hair, fur, etc.

SF is currently not believed to be carcinogenic, it has a TLV of 5 ppm and it can be dispersed into the atmosphere as long as no points downwind exceed the TLV. Typically, in the fumigation of dwellings, once the exposure is complete, the residual SF is purged into the neighborhood with a fan. Although regularly carried out, this is probably a less than ideal situation. Particularly since, with their greater volume compared to chamber fumigations, dwellings require one to two orders of magnitude more weight of SF.

SF has proven insecticidal capability for insects normally encountered in the fumigation of buildings but, for many species of specific interest to museums, SF needs research on the 100% lethal dose [LD100][11]. to ensure correct treatment. In one of the few reports of the use of SF for museums, G. Alpert[12] reports that a major US Museum was fumigated in 1985 with one 24 hour exposure to 3lbs/1000 cu. ft of Vikane for an infestation of the odd beetle, <u>Thylodrias contractus</u>. Traps set before the fumigation revealed the infestation. Since the fumigation, the traps have shown no further occurrences and no effect on the collection has been reported. Considerable care was taken to distribute the SF with multiple application nozzles and to spread it further with strategically located fans. SF diffuses rapidly, resulting in thorough penetration and adsorbs very little into the fabric of exposed objects. Dow is in the process of quantifying the residual absorption effects for the U.S. Environmental Protection Agency[13].

In spite of its wide use for building fumigation with contents in place, there is little evidence of significant adverse reactions between it and household effects. Care must be taken that the SF is in the vapor phase and that the cooling effect of evaporating droplets does not condense water vapor as dew and also that there is no surface water present, since the SF can hydrolyse to hydrofluoric and sulfurous or sulfuric acids. Although SF is believed to have

little long term effect on the chemical nature of the object, some adverse reactions can be postulated between objects and both SF and the residual impurities always present. From a recent communication[14], the manufacturing process for "Vikane" brand SF leaves a range of other compounds in the finished product. Although the manual states that up to 1.0% "inert ingredients" may be present, these seldom exceed 0.2%. These compounds include alkyl chlorides such as ethylene chloride, thionyl fluoride (SOF_2), sulfur dioxide (SO_2), hydrofluoric acid (HF), hydrochloric acid (HCl), chlorine and water vapor. For museum objects these impurities could be most significant. The use of a packed bed pre-filter of an alkaline carbonate or bicarbonate should be an efficient scrubber for the HCl and HF and have some effect on the SO_2. This concept will be actively pursued.

Already, the Getty Conservation Institute is funding work[15] at their own laboratory, at the Canadian Conservation Institute and at CAL to study the reactions of SF with a range of materials (with preliminary results due in early 1988). Until this work or some other report is presented, little can be said other than that, if the possibility of damage is suspected, it is desirable to run a test sample through the fumigator first. This, of course, would only show immediate, not long term effects.

One potential disadvantage of SF compared with EtO is that it does not kill mold spores. Since molds are always with us, the current approach is to ensure that collections have good ventilation and that local microclimates, that favor mold growth, do not occur[16]. Air conditioning that holds relative humidity to less than 65% and temperature to below 22C, effectively stops growth. Even approaching these conditions is beneficial. Gross infestations should be mechanically cleaned with due care for the object. Since fungi produce mycotoxins, the cleaners should wear masks and the dusts should be treated as any other noxious fumes. Thus, if conditions can be reasonably controlled, the loss of fungicidal action for SF is a minor disadvantage. If conditions exist that favor fungus growth, then effective fumigation will only delay the inevitable, not avoid it.

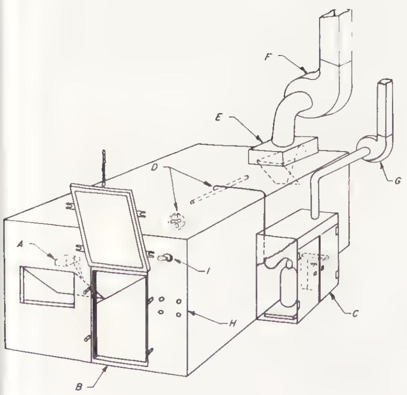

Figure 1 Fumigation Booth design from G. M. Hama.
- A. Automatic Damper closure interlocked with fan, F.
- B. Loading door
- C. Cylinder cabinet ventilated by fan G.
- D. Nozzles and fan for introducing and mixing fumigant
- E. Interlocked fan damper
- H & I Switches and lights

Facility design

The "Vikane" label instructions state; "store cylinders ... in a secured and well ventilated area away from dwellings and work areas" This avoids a lot of problems that might arise from potential leakage of the fumigant. Full, partially used and empty cylinders that are in storage are covered by this mandate. It should be noted that fumigant and pesticide label instructions are legally binding and not just advisory in the USA.

A fumigation facility should be put in a separate building if there are no constraints from existing structures. "Industrial Ventilation, a Manual of Recommended Practice"[17], reproduces a layout, first appearing in a thorough paper by G. M. Hama[18], that shows a schematic ventilation chamber. This can be seen in fig 1. The cylinder that supplies the fumigant is shown in a positively ventilated cabinet inside the facility. Since the location of the cylinder in active use is not specified on the label, this arrangement is a prudent one that follows good safety practice. However, in planning a new facility it would be better to have the SF delivery system on an outside wall with cylinder access from the outdoors and all connections to the main facility, including the operator door and other penetrations, with good seals.

The size of the door to the main room and the ventilating fan exhaust rate for the SF metering equipment and cylinder cabinet should be designed to provide at least 100 feet per minute air velocity through the door opening. This will protect the operator should an escape of SF occur during the addition of fumigant to the chamber. The room should have exhaust ventilation at all times to prevent SF concentration building up from minor leaks. Some form of bottle restraint such as a light harness made from aircraft control-cable or light chain should be in place that does not interfere with operation of the weighing scale used to measure the amount of SF delivered to the chamber. Immediate evacuation would be required if the bottle fell over in a facility and its valve were knocked off or otherwise damaged. When bottles are changed, the valve bonnet, which protects the valve during shipping and storage, should be in place before the bottle restraint is removed.

Whether located separately or in an existing building, the ideal facility would have a quarantined receiving area, a fumigation chamber and an airing room for treated objects, all with museum quality climate control. The chamber would act as an "airlock" between the two rooms, with a door at each end, and thus prevent reinfestation of treated material by that awaiting treatment.

In most situations this design luxury cannot be accommodated and the typical fumigation facility consists of a large room containing either an atmospheric or vacuum chamber. Objects awaiting fumigation are isolated in heavy polyethylene sheeting. Treated objects are removed to clean areas, to prevent reinfestation, as soon as absence of residual fumigant is assured.

The preponderance of commercial experience is with atmospheric fumigation, but there is a theoretical advantage in using a vacuum chamber in that the vacuum removes air from all interstices, directly replacing it with fumigant as the

pressure is restored. This contrasts with slower diffusion into narrow crevices, etc. in the atmospheric case.

Vacuum Fumigation Procedure and System Design Criteria

The procedure for vacuum chamber fumigation is to place the objects into the chamber, ensuring that all sealed containers are opened. No objects should be vacuum treated that would be damaged by the application of vacuum. Objects with sealed compartments are particularly vulnerable. The chamber is closed and the pressure reduced from the nominal 14.7 psia (pounds per square inch absolute) or 760 mm mercury at sea level to 1-2 psia. The SF is then introduced.

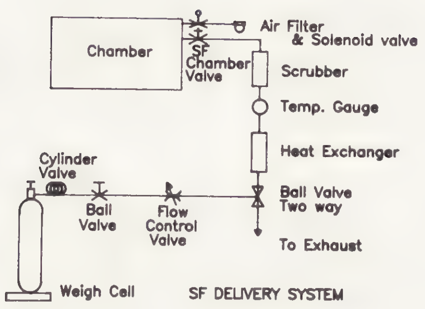

Figure 2 Fumigant supply system.

The metering system, starting at the cylinder valve, could consist of a shut-off valve, a metering valve, and a two-way valve to allow feedlines to be purged of SF after the addition. The lines between the cylinder and the metering valve should be of small diameter (1/8") to minimise the amount of excess SF over the weighed tare amount that will be added to the chamber. See figure #2 for one such design. Metering valves and compression fittings of industrial rather than plumbing quality should be used to ensure system integrity. At a nominal addition rate of 3 pounds per 1000 cu. feet, most chambers will require 0.3 to 10 pounds depending on volume. Since the cylinder initially contains 125 pounds and has a gross weight of over 200 pounds, the practice used in fumigating buildings, where the greater volume requires much larger weights of SF to be injected, of weighing out the charge with a bathroom type scale cannot be followed. An electronic scale of greater sensitivity is required to measure accurate charges of SF by difference in weight. This equipment normally comes with choice of metric or avoirdupois readout and ability to provide gross, net or tare readings. If the net weight mode is used with a good metering valve, even small additions can be made with precision.

The evaporation of the volatile liquid SF requires input of the latent heat of vaporization if liquid SF is not to reach the chamber. Many vacuum chambers were designed for use with EtO/CFC-12 mixtures and have heat exchangers installed to evaporate the much larger volume of CFC-12 . Since this fluorinated hydrocarbon has very similar physical characteristics to SF, the heat exchanger will effectively ensure vaporization of the smaller volume of SF. CFC-12, Dow Chemical trade name "Freon 12", can also be used to test equipment integrity and performance before running with SF. Very sensitive "Freon" leak detectors are available for use with refrigeration systems that can be used to ensure a leak-free system before introducing SF.

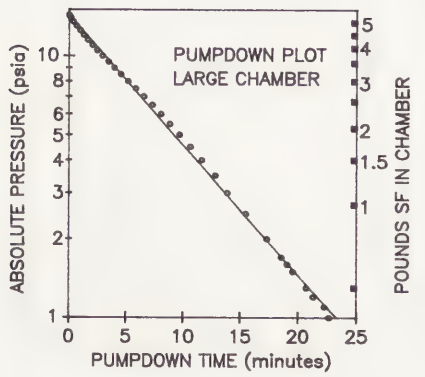

Figure 3. Pump down curve for SI large chamber. Abscissa scaled in minutes, ordinate in both absolute pressure and weight of fumigant still in chamber.

Returning to operational procedures: as described, the cylinder in use and the metering system should be in a virtual fumehood. For protection against liquid leaks, a face shield should be used when operating the valves. Evaporation of the liquid SF cools the vapor and remaining liquid to around -55C. Thus the use of gloves is inadvisable since contact with supercold SF trapped in a glove is a much greater danger than the insignificant risk of absorption of SF through the skin. If the valves chill below freezing point, "flat potholders" should be used for hand protection instead. Once the SF has been added, the bottle should be immediately closed and the purge valve opened to clear the lines into the chamber which is still under vacuum.

There is some question as to whether it is more effective to leave the objects in SF under vacuum or to backfill the chamber with room air to nearly atmospheric pressure . Consideration for the objects decrees that the backfill mode be used since the desired ambient for objects of 21C (70^{o}F) and 50% relative humidity can more nearly be attained during the 24 hour exposure time required to kill insects and eggs. Circulation fans for good mixing should be present in the chamber.

After the holding period, the contents of the chamber are pumped into the air stream of a high volume exhaust vented into a vertical stack. This stack should be designed to maximize the vertical air velocity and thus disperse the vapors thoroughly before they can be breathed directly or induced into adjacent air conditioning intake ducts. The determination of a pumping rate curve, plotted on semi-log paper to approximate a straight line, shows the rate of fumigant removal. See figure 3 for the plot for CAL's large 1785 cu. ft chamber. From these data the change in concentration of SF in the effluent gas as pumpdown proceeds can easily be determined.

To ensure thorough airing of the load, air replacement and pumpdowns must be repeated enough times to reduce residual fumigant to below the TLV. If the initial chamber pressure is 15 psia and the final pumpdown pressure is 1.5 psia, on backfill with room air to 15 psia again, the dilution will be 10%. Thus for the above conditions, starting at 10,000 ppm SF, at least four (4) pumpdown cycles are required to approach 1 ppm. Experimental runs, using "Freon", should be made to determine how many pumpdowns are required with the specific equipment and objects. Kindness to the object indicates that the number of pumpdowns should be held to a minimum.

Atmospheric Fumigation Practice and System Design Criteria

For atmospheric chambers, the cycle is very similar to that used with vacuum

equipment except that the fumigant is introduced with the chamber at atmospheric pressure. Most vacuum chambers can be used for atmospheric fumigation if the automatic controls are bypassed and the cycle manually operated.

The addition of about one percent fumigant vapor (10,000 ppm) to the existing air does increase the pressure by the same percentage so that chamber seals and shell integrity should be good. A leak of 1 cubic foot from a 100 cu foot chamber can bring 2,000 cubic feet of room air up to the TLV. The facility air conditioning must have a good air replacement rate to take care of such potential slow leaks. This is not so significant during vacuum fumigation since the chamber is always at slightly sub-atmospheric pressure during the fumigation exposure time.

Following the exposure, the purge fan, F in figure 1, is turned on and then the smaller air inlet door is allowed to open. With the high concentration of toxic vapors present, the air velocity through the air inlet should be at least 500 feet per minute to prevent back-diffusion into the room

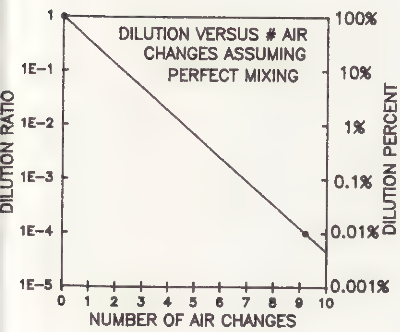

Figure 4. Concentration of fumigant during exhaustion of chamber with fresh air makeup, assuming perfect mixing. Percent residual fumigant versus number of air changes

Using Hama's model[17], during fumigant discharge, the air entering the chamber mixes with the contents. If mixing were perfect, the change in concentration would follow an exponential law such that

Cfinal/Cinitial = e-A where A = # air changes

or A = 2.303 log10(Cinitial/Cinitial)

This means that, after each air change, the concentration of contaminant would be reduced to 36% of its initial value. In practice the decrease is more gradual due non-uniform mixing and either the time or the exhaust flow-rate should be multiplied by a distribution factor of about three (3). The theoretical curve is expressed graphically in figure 4. The resulting times need to be multiplied by the distribution factor. With an initial concentration of 3 pounds per 1,000 cubic feet (10,000ppm) the required reduction to 5ppm is 0.05%. From the semilog plot, 7.6 air changes are needed with perfect mixing. As an example, for a chamber 10' x 20' x 10' (2,000 cu ft) with 60 minutes clearing time and a distribution factor of 3, an exhaust fan of

3 x (2,000 x 7.6)/60 i.e. 760 cu.ft per minute is required. Once the chamber is cleared, the main door may be opened but the fans should be left running. As with the vacuum system, the effectiveness of the calculation should be checked by some practical measurements of SF concentration.

The same calculation can be used to determine the time required to clear a contaminated area in a facility. If the spread of contaminated air to other occupied spaces by the air conditioning system is not to be a hazard, HVAC details must be investigated and modifications made if necessary for isolation.

Instrumentation

The primary instrument for the detection of organic vapors, the nose, is not effective for SF, since it has no smell. In the fumigation of buildings, an initial charge of chloropicrin at about 20ppm, as a pungent warning agent, is used to assure that the space is free of people, pets, etc. No tracer is available for mixing with the SF itself. Thus constant care and good, well maintained instrumentation are the only safeguards for detecting inadvertent releases of fumigant.

Analytical equipment should be available both to check the nominal 10,000 ppm fumigant concentration in the chamber during fumigation and to measure in the 2-30ppm range to comply with the 5 ppm TLV criterion for checking both objects after treatment and the facility surroundings. The Dow "Vikane" Fumigation Manual[8] recommends instrumentation for both classes of use.

For checking chamber concentrations, Dow recommends the "Fumiscope", an instrument using thermal conductivity as the measured variable. The principle of operation is that when SF of molecular weight 102 is mixed with air of molecular weight 30, the effect of even small differences of concentration on thermal conductivity can be measured. This can also be used for CFC-12 in similar concentrations, if it is used for testing.

For measurements in the TLV range, either "Interscan" or "Miran" instruments are advised. The "Interscan" pyrolyzes SF to sulfur dioxide (SO_2) which passes to an SO_2 sensor The readout is directly in ppm SF. The "Miran" is a portable infrared (IR) spectrometer which measures the IR absorption at one particular wavelength. Some other compounds, particularly ethyl alcohol, adsorb less strongly in the same frequency band, causing potential false readings, particularly in chemical facilities. Care should be taken that this effect does not cause problems of false, high readings.

In addition to their portable equipment, the Foxboro Company produces an automatic, twelve (12) sampling point "Miran" device using the same basic spectrometer. One sampling point is devoted to automatic zeroing and a second can be used to connect a bottle of prepared 5ppm SF mixture with air through a demand regulator for instrument calibration. This leaves ten potential sampling points. Since sampling points can be easily included or omitted, checking calibration or using a sampling tube for checking newly opened

chambers or recently exposed objects is easily carried out. The equipment also comes with a multipoint chart recorder and two programmable warning levels. Thus a suitable automatic warning can be given of SF leaks and differentiation made between minor and catastrophic events. For reliable use and avoidance of false warnings, the equipment must be regularly calibrated and the use of solvents, particularly ethyl alcohol, avoided near any of the sampling points.

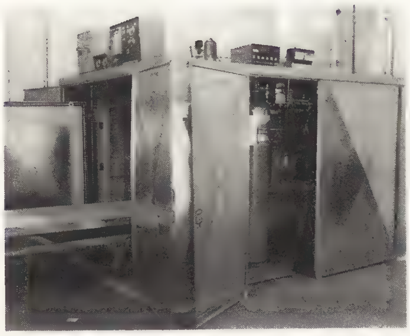

Figure 5. CAL small fumigation chamber with ventilated housing. Vikane bottle and fumigant supply system under housing

General design and procedural comments

Unless plans and protocols are available that have been thoroughly reviewed and that meet local regulations, the services of a chemical engineer should be obtained to design the facility and its "Vikane" delivery, dispersal, measurement and ventilation system. Written procedures for its operation and safety procedures, including disaster plans, should be worked out between the engineer and a conservator. Coordination with museum security, pesticide regulatory authorities, industrial hygienists and the local fire department should also be included.

The person in charge of the facility should have some knowledge of chemistry and certainly an extensive knowledge of conservation. The actual operator should have at least a high school diploma and carry out operations under the direct control of the person in charge. Operators need to be well trained in the operation of the facility due to the toxic nature of the fumigant, the potential for harming objects particularly if contacted by liquid fumigant, and the possibility of not fumigating if objects are packaged in impermeable containers. No formal training is known for fumigators other than short courses that are offered from time to time and those designed to train for a pesticide operators license. In the USA, this licence is required for all persons responsible for such facilities and, in many jurisdictions, formal operator training must be carried out by the person holding the fumigator's license.

Figure 6. CAL large fumigation chamber. Control console on right. When closed, door drops into alignment with hydraulic action and is cammed closed to ensure leaktight fit.

As Monro points out, fumigation only kills at the time of fumigation. It has no long term residual biocidal properties. Good "housekeeping" is the only effective and safe way of preventing insect and fungal growth. Particularly in warm climates, even air conditioned air carries new mold spores than will start new growth if the environment is right. It only slows things down to kill the spores already present on the object. Buy good storage conditions rather than trying to correct the wrongs occasioned by bad ones. For the occasional requirement, find a good commercial fumigator to carry out the fumigation.

The CAL facility at the SI Museum Support Center

The Conservation Analytical Laboratory has the responsibility for setting up and operating a fumigation facility at the SI Museum Support Center (MSC). This Center was designed to house objects from the collections of the SI, particularly of the National Museum of Natural History (NMNH). MSC has more than 300,000 square feet (30,000 m^2)of storage in addition to another 150,000 square feet (15,000 m^2) devoted to associated laboratories and offices for curators and conservators. The building is located in a parkland site, and laid out for easy access to the over 6,000,000 objects. CAL is one of the tenants occupying 25,000 square feet (2,500 m^2).

Planned ten years ago before sensitivity to fumigant problems became significant, the 40 foot (12 m) by 40 foot fumigation facility is located adjacent to the MSC loading dock. This facilitates treatment of incoming infested objects. It is air conditioned to the Support Center specifications of 70+/-2^{o}F (21C) and 50% +/-2% relative humidity. At one time, all objects entering MSC were to be fumigated before storage. With enhanced concern for the object, incoming material is now subject to careful inspection and only fumigated if infested.

7. On left, Miran, twelve point SF detector with standardizing bottle of air/SF mixture. Ventilation control console on right with status controls and indicating lights at top of panel, damper status lights in middle and fan status lights at bottom. "SF Present" warning light at top left and 72 dB klaxon at top right.

The facility has two vacuum fumigation chambers, one of 100 cu. ft with 3'-6"w x 7'-6"l x 3'-0"h, usable space, figure 5, and the other of 1782 cu. ft with 9'w x 22'l x 9'h space, figure 6. MSC will house many large objects such as totem poles and whale bones from NMNH's ethnographic and zoological collections and required the installation of such a chamber.

The smaller chamber is covered with a sheet metal housing that also contains the cylinder of SF and the metering valves for both chambers. The cylinder is secured with an aircraft cable harness to prevent its falling over and damaging the valve. The housing is continuously ventilated and monitored with one of the (12) sampling points of an automatic "Miran" IR spectrograph set to detect SF down to less than ½ ppm, figure 7. A control system provides automatic response of the ventilation system to intended changes during fumigation cycles and also monitors for unusual SF concentrations. For instance, should there be fan failure, the loss of fan pressure differential in the ducting automatically turns on one of the other fans in the system and opens and closes dampers appropriately. The control system then indicates the failure to plant engineering personnel for urgent correction. Indicator lamps show the condition of all three fans, all eight dampers and the various configurations of the system. Should electric power be lost at MSC, the detection, control and ventilation systems are all moved to emergency generators.

When the system is between fumigations, the SF cylinder valve is kept closed and the cylinder and metering valve enclosure is positively ventilated and monitored by the "Miran". The whole facility is ventilated with a higher proportion than normal of makeup air. The system is not tied in with any other HVAC systems in the building.

When either chamber is run, the conditions above prevail until the SF addition is to be made. At that time a further fan is activated that ensures over 100 feet per minute flow across the SF enclosure left hand access door (fig 5). The right door is kept closed to minimise the opening cross-sectional area. The SF cylinder valve is turned on and the metering valves used to make the appropriate addition to the chamber under vacuum. All valves are then closed and the line into the chamber, which is still under vacuum, purged of SF . Conditioned room air is admitted to the chamber until the pressure is slightly under atmospheric (13.5 psia). The control system then closes the chamber solenoid valves, which in any case go to the closed position with lack of power. During the insect killing exposure period, the ventilation system reverts to the lower flow rate standby condition to keep ambient conditions in the facility at optimum. At this time, all SF is either in a closed cylinder or else in a vacuum vessel with vacuum tight seals under slight negative pressure.

At the completion of the exposure cycle the automatic chamber cycling controls do not proceed further until an operator using a keyed switch (as are most switches in the system to prevent unauthorized use) initiates the pumpdown phase. After checking wind conditions and informing appropriate security and plant engineering staff, the switch is closed to continue the automatic cycle. The larger exhaust fan starts once more. After 20 seconds delay to develop flow in the exhaust duct, the chamber vacuum pump is turned on to discharge SF into the exhaust stream. Wind speed and direction indicators are installed for the facility. In addition, the discharge system has been checked with titanium tetrachloride derived smoke. This was induced into the exhaust under the full range of wind conditions to ensure that effluents are not reintroduced to the building by the ventilation intake ducts.

The location of the fumigation facility adjacent to loading dock, receiving and office areas gave extreme concern for the protection of staff from possible leaks. The automatic "Miran" through the controller of the exhaust system is capable of putting the facility under negative pressure should any SF release be detected. This should prevent escape of SF into the surrounding occupied areas. The system is triggered at a conservative 3ppm in the facility itself and starts the ventilation system at a high exhaust rate. It also gives an audible warning. Should the level in the facility exceed 50 ppm or in any of the surrounding occupied areas exceed 3 ppm, this is taken as an indication that the system has been overwhelmed by an SF release. This is serious enough to be the cause for evacuation of the building. At this time, klaxon horns throughout the MSC would be sounded.

From the above description of operating procedures, it can be seen that serious leakages of SF are highly unlikely. False triggering of the detection systems is a much more likely cause to initiate alarms. A section of the operational manual for the system is devoted to emergency procedures to deal with such unlikely events. Frequent standardization is mandated to ensure proper instrument performance. Routine drills, including the use of the self- contained breathing apparatus, needed to enter a building with SF above the TLV, are part of the price of not having a stand-alone facility.

Setting up a facility of this type involves active cooperation from all members of the museum community. The author recognizes the significant contributions of these colleagues in developing such understanding as we have been able to attain.

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SUMMARY

A study on the ultrastructure of the 11th-19th centuries parchment scrolls of different degrees of destruction has been carried out. It was shown that parchment is composed of tightly packed bundles of collagen fibrils with characteristic periods and subperiods. Fibrils are cemented together with an amorphous interfibrillar material containing rutheniofile compounds. Two types of alterations were found in parchment samples: the formation of cracks between bundles of fibrils, and disintegration of fibrils as a result of the lytic activity of microorganisms. With a view to investigate the alteration in the structure of collagen of medieval parchment, its stability against the effect of proteases (collagenase, trypsin, chymotrypsin, papain and pepsin) was also tested, showing that the hydrolysis of parchment was caused by both specific and non-specific proteinases.

ELECTRON MICROSCOPIC AND BIOCHEMICAL INVESTIGATION OF PARCHMENT

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1. Introduction

In order to create optimum storage conditions for ancient manuscripts and documents on parchment it is important to know the causes of its destruction. Parchment served as the most common material for writing and as the base of miniature painting in the Middle Ages. It was manufactured from animal skins - mainly from those of calves, goats and sheep. The principal constituent of the animal dermis is the fibrillar protein collagen. After the removal of hair from animal skin, collagen constitutes are over 90% of dry substance of dermis (by weight).

The collagen molecule consists of the helical association of 3 chains and has a molecular mass of 300,000 daltons. It is 280 nm long and 1.4 nm thick. The molecules are combined into fibrils which are a primary form of the submolecular structure of collagen. Electron microscopy of native collagen fibrils of using negative colouring or positive contrasting demonstrates the periodicity of fibrils (the period is 64-67 nm long and it consists of light and dark zones). One of the hypotheses accounting for the cross lining of fibrils is a shift model of neighbouring collagen molecules by one quarter length (1, 2).

The level of collagen arrangement, following fibrils, is represented by fibres consisting of a large number of fibrils, and observable in a light microscope. Collagen fibres are submerged into the principal substrate playing the role of interfibrillar cementing material. Its main chemical components, proteins and polysaccharides, combine to form complex compounds of different molecular structure and stability (proteoglycanes and glycoproteins).

2. Electron Microscopic Examination of Parchment

The physical properties of parchment depend mainly upon submolecular collagen structures which are known for their high resistance to the effect of environmental factors. This is confirmed by the excellent preservation of many medieval manuscripts on parchment. However, changes in the physico-mechanical and physico-chemical properties of medieval parchment are well known to occur even upon storage under favourable conditions. The changes concern tensile strength, temperature of hydrothermic shrinkage, moisture absorption and pH. An electron microscopic examination was conducted to study the ultrastructure of parchment samples of varying ages, the manufacturing techniques and different degrees of preservation, and to detect submicroscopic alterations. The parchment scrolls under investigation included Greek (11th-12th centuries), old Russian (14th-15th centuries), German (13th-14th centuries), West European manuscripts (16th-17th centuries), a torah dating from the end of the 18th or the beginning of the 19th century, and, also, modern parchment hand-made of a suckling calf skin at the "Moskozhobjedinenije" plant for restoration purposes.

Parchment pieces of up to 1 mm^2 in size were fixed in 2% OsO_4 solution in 0.1 M cacodylic buffer, pH 7.3, for two hours and dehydrated in alcohols of increasing concentrations. Some samples were fixed in a 3% solution of glutaraldehyde in 0.1 M phosphate buffer and then in 1% OsO_4 according to Coulfield. In the course of dehydration, the samples were treated with 3% uranyl acetate. A part of samples, with a view to selective staining of parchment components containing carbohydrate, were fixed in OsO_4 solution with an addition of rhutenium red. The dehydrated samples were placed in Araldite. Ultrathin sections were successively contrasted with a 3% solution of phosphoric tungstic acid and lead citrate according to Reynolds. They were then examined in the electron microscope JEM-100 S with three to five thousand times magnification.

The treatment techniques of preparing for the electron microscopic examination of animal and human dermis turned out to be quite suitable for parchment as well. All examined parchment scrolls had an identical ultrastructure, i.e., consisted of more or less tightly packed bundles of collagen fibres. Elastic fibres connective tissue cells and their remnants, as well as remnants of epidermis were not found in parchment material.

Characteristic periods and subperiods of collagen fibrils were detected in all parchment scrolls with the exception of the considerably destroyed parchment of the 11th century (Greek manuscript). This is an evidence of the great stability in time of submolecular collagen structures. The thickness of fibrils ranged from 80 to 90 nm, and the length of periods was within 54-56 nm (Fig. 1). In general, the more numerous the areas where collagen fibrils exhibit distinct periods and subperiods, the better is the preservation of the parchment, as estimated organoleptically.

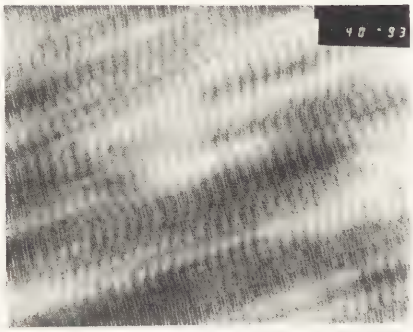

Figure 1: A well preserved 13th century parchment; periods with 10-12 subperiods are seen distinctly. Maginification 40,000X.

Rhuteniofile material was present in all the samples. It is closely linked with collagen fibrils and forms on their surface a sort of belt pattern, repeating the periodicity characteristic of fibrils. Amorphous interfibrillar component of parchment is also rhuteniofilic. The data on electronic density and the presence of rhuteniofile matter indicate that the composition of the amorphous cementing material includes proteins, proteoglycanes and, possibly, glycoproteins.

Two types of changes were observed in medieval parchment scrolls. The type 1 change is characterized by cracks between collagen bundles (Fig. 2). They may have appeared due to parchment drying up. The type 2 change is the destruction of collagen fibrils as a result of the lytic activity of microorganisms: bacteria and micromycetes (Fig. 3). Next to the colonies of microorganisms there are accumulations of amorphous material and collagen fibrils at various stages of disintegration. Prior to disintegration, collagen fibrils undergo microfibrillar destruction.

The two types of changes sometimes accompany each other, but in some parchment scrolls were seen only cracks.

3. Biochemical Investigation of Parchment

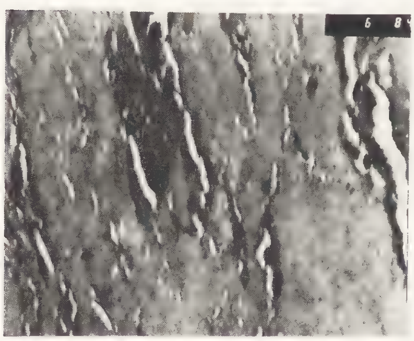

Figure 2: Cracks between collagen fibril fasciles. Magnification 6,000X.

An important indicator of the preservation of the collagen molecule is the degree of its resistance to the action of the proteolytic enzymes. It is only a collagenese-like enzyme that can hydrolyze peptide bonds in the helical areas of undenatured collagen (3). However, various treatments (moderate heating, treatment with acid and alkaline solutions) lead to collagen denaturation. During the denaturation weak non-covalent bonds, maintaining the regularity of the polypeptide spirals of collagen, break up, and spirals are transformed into chaotic balls. Denatured collagen may be hydrolyzed by non-specific proteases. It may be suggested that collagen structures of medieval parchment were partially denatured in the course of the processing during the manufacturing, and also by the natural weakening of bonds between peptide spirals as a result of long-term storage, which is demonstrated by alterations in its properties. The destruction of the amorphous cementing substance seems to occur during the ageing process. An investigation was conducted of the stability of parchment samples of different ages and the degree of preservation against the action of proteases in order to determine the degree of collagen denaturation.

Samples of manuscripts on medieval parchment of the 12th century (badly conserved), 17th century (satisfactorily conserved) and modern parchment were subjected to hydrolysis by trypsin, chymotrypsin, papain, pepsin and collegenase. The samples of air-dry parchment (10 mg.) were powdered in a porcelain mortar with 0.5 ml. 0.01 M Tris HCl buffer pH 7.6, containing 3% $CaCl_2$, and some of the samples, with, 0.5 ml. citrate buffer, pH 2.0. To the suspensions obtained was added 0.1 ml. of the enzyme solution containing 200 mcg. of the preparation. The samples were subjected to 24-hours hydrolysis. The amount of amine nitrogen (4) was ascertained in the supernatants after centrifugation (8000 r.p.m., 15 min). The enzyme preparations used in this study (trypsin, chymotrypsin, papain and pepsin) were the products of SPOFA. Collagenase was isolated from the culture medium of Clostridium hystoliticum in the Institute of Biological and Medical Chemistry of the USSR Academy of Medical Sciences.

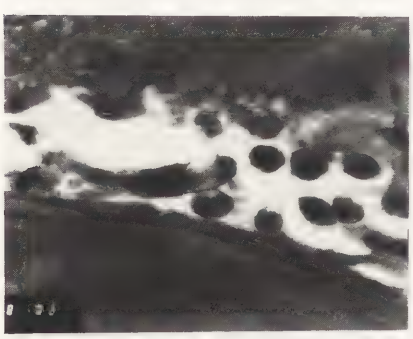

Figure 3: Bacteria in a crack between fibril Fasciles. Magnification 20,000X.

Structural alterations in medieval parchment collagen were determined by the amount of acid-soluble and salt-soluble collagen, as compared to that in modern parchment. For that purpose, to one half of the parchment samples was added 0.01 M Tris-HCl buffer, pH 7.6, containing 3% $CaCl_2$ in the amount of 0.5 or 2 ml. depending on the size of the sample (neutral-soluble); to the other half of the samples, citrate buffer, pH 3.8 (acid-soluble) was added. Samples were powdered in a porcelain mortar and left in the refrigerator for 48 hours, then centrifuged at 8,000 r.p.m. for 15 minutes. The supernatants obtained were subjected to an acid hydrolysis, and then the content of hydroxyproline was determined by the dimethyl aminobenzaldehyde micromethod (5). The corresponding buffers were then added to the precipitates and a repeated determination of hydroxypoline in the supernatant was carried out after 240 hrs. The results of this experiment are presented in Table 1.

The content of acid-soluble and neutral-soluble collagen, as well as the quantity of peptides and amino acids in medieval parchment, as compared to modern parchment, was investigated. These data provide additional qualitative characteristics of collagen structures of medieval parchment. The content of neutral-soluble collagen was several times higher than that of acid-soluble

Parchment scrolls	Weight (mg.)	pH	Sol. collagen(mg.) Determ. 1	Sol. collagen(mg.) Determ. 2	Sol. coll. in %
1. 17th cent. manuscript	10	7.6	0.1094	0.0530	1.62
	10	3.8	0.0213	0.0388	0.60
2. Greek man. 12th cent.[x)]	5	7.6	0.0372	0.0380	1.50
	5	3.8	0.0190	0.0097	0.57
3. Greek man. 12th cent.	5	7.6	0.0251	0.0286	1.07
	5	3.8	0.0144	0.0045	0.38
4. Greek man. 12th cent.	10	7.6	0.1201	0.1238	2.44
	10	3.8	0.0327	0.0134	0.46
5. Bind. parch. 18th cent.	50	7.6	0.1626	0.0492	0.42
	50	3.8	0.5282	0.0947	1.25
6. Modern parchment	50	7.6	6.5550	0.0828	13.28
	50	3.8	0.3648	0.1059	0.94

[x)] No. 2,3 and 4 are fragments of sheets of one manuscript.

Table 1

Content of Acid- and Neutral-Soluble Collagen in Parchment Samples

collagen in all parchments studied with the exception of binding parchment. The content of neutral-soluble collagen in medieval parchment ranged from 1.07 to 2.44%. The maximal amount of neutral soluble collagen was found in modern parchment (13.28%). Decrease in content of neutral-soluble collagen in medieval parchment was due to changes in chemical bonds in collagen fibrils and to denaturation processes in collagen leading to the loss of solubility of this protein.

The degree of parchment resistance to the action of proteolytic enzymes was judged by the amount of soluble amine nitrogen after hydrolysis as compared to the control (Table 2).

The figures given in Table 2 were defined as a mean value of three determinations carried out at different times, each determination consisting of two parallel experiments. The minimal variation coefficient was 11%, the maximal 29%. The high level of the variation coefficient was due to the heterogeneity of the material under investigation.

In spite of the difference in absolute figures, a stable dependence of the level of parchment hydrolysis by collagenase on the extent of its destruction was maintained in all repeated experiments. The amount of amino acids and soluble peptides in the samples of the 12th century parchment (poor preservation) was increased eight times; in the samples of the 17th century documents, three times. Considerable resistance of modern parchment to collagenase action was possibly connected with a protective function of the interfibrillar amorphous substance. Pepsin (acid protease) did not affect the parchment under investigation. Other proteases hydrolysed parchment approximately to an equal extent.

Enzymes	pH	Greek manuscript 12th century	Instrument 17th cent.	Modern parch.
Control	7.6	103.5	76.0	38.3
Collagenase	7.6	828.5	240.0	67.8
Trypsin	7.6	194.2	120.0	110.0
Chymotrypsin	7.6	144.7	108.0	80.2
Papain	7.6	113.8	100.8	101.7
Control	2.0	10.0	-	21.6
Pepsin	2.0	6.0	-	25.2

Table 2

Resistance of Modern and Medieval Parchment to the Action of Proteolytic Enzymes (mcg of tyrosin per mg of parchment)

The extent of parchment destruction can be judged by the amount of soluble peptides and amino acids in the control samples (pH 7.6) to which the enzymes were not added. The control level of 12th century parchment samples (poorly preserved manuscript) was nearly three times higher than that of modern parchment.

These data show the remarkable durability in time (from 3 to 10 centuries) of collagen structures in parchment. This durability could possibly be explained by the stability of supermolecular structures of collagen as confirmed by electron microscopic studies.

The investigation carried out demonstrates that the employment of electron microscopic and biochemical techniques makes it possible to determine alterations in structural elements of parchment material on which conservation of parchment manuscripts and documents depends, and to find out the main causes of their destruction.

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UMMARY

onuments exposed to the pen air often show alter- tions caused by the de- elopment of vegetal bio- leteriogens which must be liminated during restora- ion. Chemical products re preferred nowadays to echanical-manual inter- ention methods. These reatments enable faster nterventions on larger reas, using less energy; hey can however have egative secondary effects y causing chemical reac- ions with the stone mate- ial. After having estab- ished their suitability s far as toxicity and nvironmental pollution is oncerned, both the effi- iency and the non reacti- ity with the substrate of hese products should be ested. This paper pre- ents the intervention rocedures for the elimi- ation of biodeteriogens ased on laboratory tests nd field experiments car- ried out on "Il Colosso ell'Appennino" by Giambo- ogna.

PROCEDURES FOR THE ELIMINATION OF VEGETAL BIODETERIOGENS FROM STONE MONUMENTS

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Introduction

The development of vegetal organisms, and in particular vascular plants, often occurring in monuments situated in rural zones or monuments that are not regularly maintained, can compromise both the vision of the monuments and their conservation. The root - system, the expansion of which varies greatly from one species to another, can cause lesions in the masonry resulting in the spalling or detachment of plaster. The aerial vegetative system causes a visual obstruction of the monument and secondarily an increase of water stagnation and of the air's relative humidity.

The "Colosso dell'Appennino" chosen to illustrate this kind of problem, is a monumental statue (medium height 10 m., circumference at the base about 40 m.) situated in the romantic park of Villa Demidoff (Florence) erected by Giambologna in the XV° century. The statue has an internal brick structure modelled on the outside with mortar to represent an old man bending forward. Due to both its environment and lack of regular maintenance it presents a fairly visible growth of spontaneous plants. Various populations ranging from lichen and algal types to vascular plants are represented in this flora.

The aim of this study is thus to identify an appropriate method to eliminate vegetal biodeteriogens present on monuments.

Methodology

The research was led along the three following areas:
A - floristical and phytosociological survey;
B - individuation of biocides and laboratory tests on their applicability;
C - in situ comparative treatments of the chosen products and evaluation of their efficiency related to different ways of application

A - Vegetation survey
The aim of this research is to acquire a better knowledge of the qualitative and quantitative composition of the vegetation and interpret its dynamism and relations with environment. These releves were carried out choosing four representative zones and following the phytosociological methodology of the Zurigo-Montpellier school.

B - Biocides
Different biocides have been selected (Table 1) on the basis of some relevant characteristic for their use in this field. Biocide products used for controlling obnoxious vegetation on monuments should necessarily present, even in the long term, sufficient guarantees of non reactivity with the substrate as far as decomposition products are concerned. This aspect of the problem which is often ignored is particularly important when operating on monuments of great artistic and historical relevance. The literature concerning this subject being very poor it has been practically impossible up to now to properly evaluate the interference with the substrate. A first indication can be obtained by the chemical composition of the biocide formulate and by its probable decomposition mechanisms.

Some tests, such as I.R. spectroscopy before and after irradiation with U.V rays (100 hours at 30 cm below two TUV15

TABLE 1 - Products choosen

active principle	class	trade name	spectrum of action	mechanism of action
1 Picloram	pyridine	Unirain	shrub	interference with the growth (hormonal)
2 Hexazinone	triazine	Velpar L	broad	interference with the photosynthesis
3 Secbumeton Ter-butylazine	triazine	Primatol 35-88	weeds	interference with the photosynthesis
4 Glifosate	organic phosphor	Spasor	weeds	inhibition of the synthesis of aromatic
5 Fluometuron	ureas derivatives	Lito 3	mosses	interference with the photosynthesis
6 Benz-Cl*	quaternary ammonium salt	Benzalconio cloruro	mosses	interference with cell membrane exchanges

*Alkylbenzyldimethyl-ammoniumchlorid

Philips lamps) and pH control of water solution (3%) of the commercial products, were carried out to obtain more informations on their chemical behaviour.

Furthermore the different biocide solutions selected were applied with brush on various kinds of stones in quantities more or less 10 times higher than those suggested for agricultural use, in order to check possible reactions or changes in colour (macro and microscopical control). More specifically samples of mortar, brick, marble, travertine and "peperino" were chosen, materials that are usually found in areas were intervention against these vegetals is particularly frequent.

C - In situ treatments
In late spring 1986 13 different experimental treatments were carried out taking into account the following variables :
- type of vegetation
- type of product
- application method

The efficiency of the treatment was regularly checked over a period of about 120 days. All the products were sprinkled directly onto the leaves, until they dripped, in water solution of 2-3 %.

In the case of wood vegetation such as elm (Ulmus minor) or ivy (Hedera helix), different application methods were also appraised. Velpar L and Unirain were applied in a mortar mixture on the cut trunk at the level of the root (about 5 ml of the solution). Furthermore the product Unirain was directly injected into the xylematic flow system through a hole pierced in the trunk (a total of 20 ml of the solution with repeated applications).

The experimentation of these methods as an alternative to sprinkling enables, when positive results are obtained, to implement treatments avoiding or limiting the contact between the product and the substrate and thus its dispersion into the environment.

Results

A - Obnoxious vegetation present

The spontaneous vegetation present on the "Colosso dell'Appennino" is a clear reflection of the climatic and soil conditions of the monument itself. The phytosociological releves essentially reveal the superposition of two types of vegetations pertaining to the Querco-Fagetea class and Asplenietea rupestris class. The first one, represented by wood mesophile clusters of trees with caducous leaves, is to be put in relation to the climatic condition of the "Park of Villa Demidoff", transition zone between meso-mediterranean and sub-mediterranean climate. The second is to be put into relation to the compact and little evolved lapideous substrate and is typical of the rupicolous formations. A third, less important, group in this context, is represented by some species of Quercetea ilicis a class of mediterranean thermophile sclerophyllas species that should also be put in relation to the climatic condition that still allows some mediterranean characteristics.

B - Control of biocides

The results of various tests are shown in Table 2. None of the products showed chemical reactions, under macro and microscopic observation, when applied on samples of the various lithotypes. The Lito 3 and Primatol products left a white deposit after water evaporation; the eventual secondary reactions that could occur after a lapse of time should still be evaluated.

No significative changes occurred in the I.R. spectra of the various biocides after they were exposed to U.V.irradiation even though a small change in colour (yellowing) of the Spasor and Lito 3 products did show. This phenomenon is enhanced for the Unirain and Ben-Cl products.

TABLE 2 - Control of some characteristcs of the biocides in water solution (3%)

Biocide	pH of water sol.	modification after exposure to U.V. radiations		behaviour when applied on specimens of various stones°	
		composition	colour	time 0	time X
1 Picloram	6,5	n.d.	drab yellow	-	t.p.
2 Hexazinone	8,0	n.d.	un.	-	t.p.
3 Secbumeton Ter.butilazina	7,5	n.d.	un.	white deposit*	t.p.
4 Glifosate	5,0	n.d.	light yellow	-	t.p.
5 Fluometuron	6,7	n.d.	light yellow	white deposit*	t.p.
6 Benz-Cl	7,2	n.d.	drab yellow	-	t.p.

° Mortar, Marble, Brick, Travertine, Peperino

n.d. = non detectable; un = unchanged; t.p. = tests in progress

* Visible only on Brick and Peperino

The control at different time intervals of the efficiency of the various treatments is shown in Table 3. Velpar L is efficient on shrubs, grass and mosses whether sprinkled or applied directly onto the root crown in a mortar mixture. Unirain was not very efficient when used as a leaf herbicide for shrub vegetation, however, it gave good results for grass and when injected directly into the trunk. When applied in a mortar mixture this product did not give positive results. Primatol 35-88 proved a

good herbicide but had a drawback, forming a white patina due to the powder deposits, this however disappeared after a few days. Spasor proved a good herbicide without any macroscopic negative effects on the substrate. Lito 3 and Benz-Cl which were chosen for treating mosses also proved to be efficient.

TABLE 3 - Experimental treatments performed on the "Colosso dell'Appennino". Control of their efficiency as a function of time, mode of application and type of organism

active principle	treatment n°	mode of application	applied on	efficiency after days: 7	25	80	120
1 Picloram	1	spray	Hedera helix L.	-	-	-	-
			Ulmus minor Miller	+/-	+	+	+
			Parietaria diffusa Metz	+/-	+	+	+
	2	spray	Hedera helix L.	-	-	-	-
	3	pack	Ulmus minor Miller	+	+	-	-
	4	injection	Ulmus minor Miller	-	+	+	+
2 Hexazinone	5	spray	Hedera helix L.	+/-	+	+	+
			Ulmus minor Miller.	+	+	+	+/-*
			Parietaria diffusa Metz	+	+	+	+
	6	spray	Melica uniflora Retz	+	+	+	+
	7	spray	Hedera helix L.	-	-	+	+
	8	pack	Ulmus minor Miller.	+	+	+	+
	9	spray	mosses, ferns	+	+	+	+
3 Secbumeton/ Ter.butilazina	10	spray	Melica uniflora Retz	+	+	+	+
4 Glifosate	11	spray	Melica uniflora Retz	+	+	+	+
5 Fluometuron	12	spray	mosses, ferns	+	+	+	+
6 Benz-Cl	13	spray	mosses, ferns	+	+	+	+

* Insufficient application of biocide, the plant shows new growth of leaves after few months.

Discussion

The results of the laboratory tests indicate negative characteristic for some products. After further investigation some of these products could be rejected. In particular the value of the Spasor water solution is a little too acid (5) which could mean a possible reaction with the surface of the stones. Unirain and Benz-Cl showed a tendency to yellow after U.V irradiation indicating a change in the molecular structure, even though it has not been possible to measure this change, in a more or less near future it could lead to a loss of efficiency and the formation of potentially dangerous decomposition products.

The samples of various stones treated with the solutions of selected biocides were observed both macroscopically and under the optical microscope. A few days after the treatment no negative reactions were observed except the formation of a whitish deposit visible only on brick and peperino samples for the Primatol 35-88 and Lito 3 due to the fact that both active principles do not dissolve in water but form a suspension. All these samples are exposed to the open air but sheltered from direct rain and are regularly checked.

As far as leaf application is concerned Velpar L proved the most suitable from the point of view of its efficiency and range of

action. However for contact and within the vascular system application Unirain also proved to be efficient.

Conclusion

The results of this research suggest procedures for the elimination of obnoxious vegetation present on monuments, and indicate some suitable biocides taking into account the different application methods.

In the present state of knowledge, it is necessary to refine the analytical research methods for an objective assessment of the interference with the substrate and this both as far as the sensitivity of measurement and the choice of the appropriate instrumentation are concerned.

It must however be noted that the quantity of the active principle that will in fact soak the substrate, taking into account the dilution effect of the solvent and the leaf type application, is really minimal. Furthermore these quantities are subject to the rain that will wash them, so that, unless there are immediate chemical reactions (in which case the use of the product is to be excluded) the effects on the substrate of these treatments after a lapse of time may be considered negligible.

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THE INFLUENCE OF THE PAST HISTORY OF WOOD ON ITS INFESTATION BY THE COMMON FURNITURE BEETLE ANOBIUM PUNCTATUM DEG. (COLEOPTERA, ANOBIDAE)

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SUMMARY

The common furniture beetle is known as a wide polyphage, but it attacks wooden objects a long period of time after they have been in use. We tested a proposal if the heating and storage conditions influence on infestation fitness. Samples of a poplar wood were dried at different temperatures to determine the water absorption dependence on drying conditions. After that the samples were infested with the common furniture beetles. The evidence shows clearly the dependence of infestation on wood hygroscopy recovery degree. A theory was propounded to explain these data.

Common furniture beetle is a pest of museum objects which can develop in wooden objects made of most leaf-bearing and coniferous species. It is known that common furniture beetles attack objects long after they are put into use. The long time needed to discover these beetles in wooden objects in infested buildings is partially caused by the long life cycle of these beetles. But one can hardly explain the delay of infestation and the preference for any sample of the same species of wood. We put forward the proposal that infestation of wooden objects was influenced by the past history of wood, i.e. heating and storage conditions.

Materials and Methods: For the experiments the wood we used was poplar samples which were stored in a room with high relative humidity - 60-80% - for one year. Before the experiments the wood was not subjected to any special drying.

To define humidity and water absorption the wood was cut into samples of 30 x 30 x 10 mm in order to conduct tests according to standards [1,2]. Also non-standard samples were cut, which were 70 mm long and had a cross-sectional area of 300 m^2, with the intent of infesting them with the common furniture beetle after conducting the same tests as for the standard size samples. The samples were dried at 103 ± 2° C (standard temperature for determining humidity) and at 60°, 120° and 140° degrees C. A control group was not subjected to drying. Test groups consisted of 6 standard samples and 3 non-standard samples. Drying was complete when the weight of the standard samples became constant. After the drying, all the samples, including control group, were placed over a saturated soda solution to determine water absorption. Then non-standard samples were taken out and placed into special cages for infesting with common furniture beetle.

Experimental Data: The results of the drying for the standard samples at different temperatures are given in table 1. As expected, the higher drying temperature caused more water loss from wood samples.

After drying, tests were conducted to determine water absorption. The character of water absorption for the different sample groups is plotted on figure 1.

As shown in figure 1, at first all dried samples absorbed water quickly but water absorption of the samples dried at 120° and 140° is less than the absorption of the samples dried at 103° (standard). The samples dried at 60° absorbed less water and the control samples absorbed the least amount of water. Initial weight of the samples dried at 60° and 103° was restored in the 2nd day and for those dried at 120° and 140° it was on the 3rd day. Weight restoration was especially slow after drying at 140°.

Control samples display a more sloping curve of water absorption. It means that water absorption for these samples is more uniform. It is clear from the table that maximum weight was gained by the samples dried at 60°, the weight of the samples dried at 103° is a little less and the samples dried at 120° and 140° took much less water. Control samples absorb water roughly the same as the samples of groups I and II. The same is true of the non-standard samples.

After being tested for water absorption the non-standard samples were put into a cage with common furniture beetle to infest them. The results are shown in table 3.

As we can see from the table 3 there were appreciably fewer eggs laid on the samples dried at 120° and 140°.

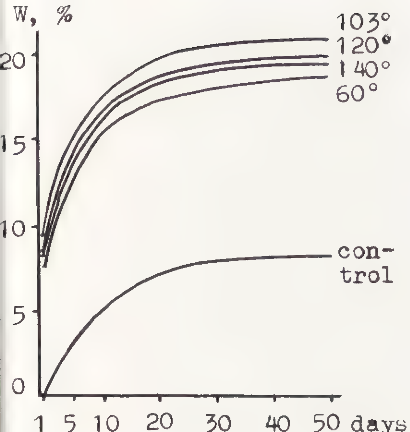

Figure 1. Water absorption diagram. The amount of absorbed water is plotted vs. time in days

Samples groups	Drying temperature, °C	Total drying time	Determined humidity W, %
I	60	11 h 10 min	9,07±0.17
II	103±2	10 h 20 min	11,46±0.10
III	120±2	10 h 20 min	11,71±0 .12
IV	140±1	10 h 00 min	12,00±11

Table 1. The humidity dependence on wood drying temperature

Groups	Drying temper-ature, °C	Average weight of samples, g		Increase of weight, %	
		before drying	after water ad-sorption tests	standard samples	non-standard samples
I	60	3.84±0.35	4.17±0.38	8.70±0.08	7.77
II	103±2	3.78±0.39	4.10±0.42	8.56±0.11	7.20
III	120±2	3.68±0.28	3.95±0.30	7.36±0.21	6.11
IV	140±1	3.71±0.13	3.96±0.14	6.76±0.05	5.70
V	-	3.90±0.24	4.23±0.26	8.35±0.06	8.33

Table 2. The influence of wood drying temperature on water absorption

The following year, the experiments were repeated for the other two groups of non-standard size samples which were cut of the same poplar wood. The samples were dried and tested for water absorption in the same manner. The results of the infestation by common furniture beetle showed the same tendency as in the previous test, namely, the rise of drying temperature resulted in a decrease in the potential for infestation. Drying at 60° did not result in a reliable increase or decrease of egg-laying in comparison with the control samples. Results are shown in figure 2.

Discussion: It now appears that intensively dried wood is infested with common furniture beetle with reluctance despite the fact that the wood absorbs more water during absorption tests than it contained before drying. Having balanced humidity before drying, the poplar contained hygroscopic water in the following fractions: almost free capillary-condensitive and poly and mono-molecular absorptive water[3]. We feel that during the drying at 60° only capillary-condensitive water is removed and then easily restored over the saturated soda solution.

To remove absorptive water one needs to use another energetic level, i.e. higher temperature. The most difficult to remove is the monomolecular layer of water, because as the water molecules and wood surface approach each other their interaction energy increases[3]. Apparently during the drying at 103°, the most mobile polymolecular water layers were removed and could be restored because the microcapillary system in the cell walls was not destroyed due to the conservation of the monomolecular layer of water, and probably some poly-molecular layers. During the more intense drying at 120°, 140° the monomole-cular layers were affected, and it is known that the rise of drying temperature decreases wood hygroscopy because only 40-50% of the initial inner surface and volume of submicroscopic capillaries can be restored[4]. When poly- and monomo-lecular layers of water are removed, the volume and probably the quantity of loosened amorphous parts of wood diminishes[4]. Upon the wood being remoistened, the absence of capillaries in a dry cell wall prevents water from penetrating inside. The water molecules must tear up the H-bonds with absorption centres on their outward surfaces to overcome the energetic barrier. So the increase of parts of crystalline cellulose hinders the wood swelling.

Changes in wood hygroscopy caused by the influence of high temperature remain constantly[5]. This can be attributed to the loss of a part of the monomolecular layer of water and in consequence to the reduction of the microcapillary system in the cell walls as well as the increase of cellulose crystallites. The authors[5] kept the wood in a relatively dry room where the relative humidity was 50-60%. If one keeps wood in a humid room, in all probability amorphous parts of cellulose are restored little by little.

We see the influence of quantity and size of the amorphous parts of cellulose on wood infestation by furniture beetle. In the proventriculus of the larvae the wood is reduced to very fine fragments[6], and this makes the contact of intestine ferments with wood carbohydrates easier[7]. Probably cellulose

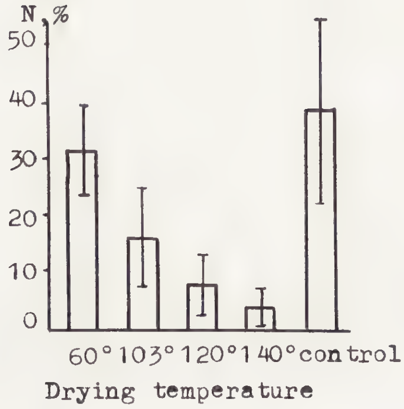

Figure 2. The dependence of wood infestation by the common furniture beetle on wood drying temperature. N is the number of eggs laid at a fixed temperature as a percentage of total number of eggs.

Groups	Drying temp-perature, °C	Number of Beetles	Number	
			of layed eggs	of born larvae
I	60	14 and 7	100	90
II	103±2		70	64
III	120±2		16	13
IV	140±1		6	6
V	-		59	52

Table 3. The results of the infestation with the common furniture beetle of wood samples after water absorption tests

crystallites without water layers are more difficult to reduce into fragments and to digest, so they are not so suitable as food for the common furniture beetle larvae.

Summary: The infestation of wood by the common furniture beetle depends on the past history of the wood. Wood dried at low temperatures (dried in the air, drying at 60°C) which does not disturb wood hygroscopy is conducive to infestation by the common furniture beetle, as soon as the wood reaches equilibrium with the environment. Wood subjected to drying that violates its hygroscopy is infested after the hygroscopy is restored (partially). It is not known precisely when wood is susceptible to infestation by the common furniture beetle. This is due to lack of information about the past history of the wood.

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SUMMARY

Herein is analysed the assemblage of chemical agents used in the USSR for protection of museum collections from keratin-destroying insects (Dermestidae, Coleoptera; Tineida, Lepidoptera). Also are characterized reliable agents which can be applied for such purposes. This article describes the particulars of main species of dermestidae and discusses those measures which aim at prevention of museum collections infection and at repulsion of destructive insects. This report represents the section of the newly published manual in shortened form Authors are: Rossolimo O.L., Pavlinov I.J., Zaitseva G.A. The name of publication: "Mammaliological collections of the USSR. Storage principles and methods." Publishing House of the Moscow State University 1986, 157 p.

CHEMICAL MEASURES OF PROTECTING USSR MUSEUM COLLECTIONS AGAINST KERATIN-DESTROYING INSECTS (COLEOPTERA, DERMESTIDAE; LEPIDOPTERA, TINEIDAE)

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The most important groups of insects injurious to ethnological, natural science and other types of museum exhibits are leather-eating beetles (Order Coleoptera, Family Dermestiidae) and moths (Order Lepidoptera, Family Tineidae). These are winged insects which show complete metamorphosis. That is, adults and larvae greatly differ morphologically. Larvae (called caterpillars for butterflies) have, in the majority of cases, a vermiform (worm-like) body. The growth of larvae is accompanied by moults, which is when the old skin, which prevents growth, splits, is cast off, and a new stage with a new skin emerges. This moulting can take place many times in the development or growing of an insect before reaching adulthood. Adults do not moult. The presence of such skins in repositories and storage cabinets is a typical indication that collections are infested by insects.

Pests proper of keratin and collagen containing materials (fur, leather, horn etc.) are larvae. Adult dermestid beetles and moths usually do not attack these materials. Most of them do not feed at all. Moths, for instance, are aphagi, their only functions being propagation. Adult Dermestidae injurious to keratin-containing materials (specimens of genera Anthrenus Schaeff., Attagenus Latr. for example) usually feed on flowers of the rose and umbellate families (Rosaceae, Umbelliferae). Specimens of some species can lay eggs of full value without being fed, i.e., they are facultative aphagi. Only adult beetles of genus Dermestes L. feed on the same materials as larvae (raw leather etc.).

The majority of pests damaging museum exhibits have a preference for natural food. However, when this is not present the dermestid larvae can devour food normally not eaten, thus widening the sphere of materials being damaged. The microclimate of museums and abundance of food substrates form favourable conditions for the prosperity of these insects in collections and becomes a foundation for their mass propagation.

Natural sources of insect pests which damage museum exhibits are bird-nests and burrows of animals.[1]

Major pests of collections belong to the following species: Anthrenus picturatus Sols., An. verbasci L., An. scrophulariae L., Attagenus smirnovi Zhant., At. pellio L., At. unicolor Brahm., Dermestes lardarius L., for beetles and moths: Tineola bisselliella Humm., Tineola furciferella Zag., Tinea pellionella L.

Chemical measures used to prevent and treat infestations in collections may be divided into two groups: a) substances destroying insects - insecticides; b) substances capable of influencing the behavioral responses of insects such as repellents, antifeedants and attractants.

Insecticides belong to many classes of chemical compounds, are not applied in the same manner, and differ in their action on the insect target. They may as well be entire or selective in their action. The use of insecticides in collections should be selective; that is, the chemical used should work only on the target pest.

In past years, the average toxicity, which is expressed as the LD_{50} (Lethal Dose 50%), of insecticides used in our country has been reduced considerably: in 1965 it was 200 mg/kg, in 1975 - 980 mg/kg. This was achieved chiefly by substituting highly toxic and persistent as well as cumulative organochloride compounds (DDT, chlordan etc.) for organophosphorus preparations which decompose into nontoxic metabolites. To protect collections, insecticides belonging to the following classes are used: organophosphorus, organochloride and synthetic pyrethroids. Of these, organophosphorus compounds are most preferred. They make up 39% of the total amount of insecticides used.

As to chemical structure, they are used in the form of:
- ethers of phosphoric acid;
- ethers of thiophosphoric acid;
- ethers of dithiophosphoric acid;
- ethers of phosphonic acid.

Substances with different organic structures which contain chlorine belong to organochloride compounds. One particular feature of organochloride compounds is their ability within the environment. To protect exhibits, the following compounds are most often used: hexatocs=hexachloran, gamma-isomer hexachloran=lyndan, paradichlorbenzene=PDB, carbon tetrachloride. At present, the manufacture of insecticides of the synthetic pyrethroid group is being developed and their use is widening. Their particular properties are selective action and low toxicity to warm-blooded animals. Synthetic pyrethroids decompose in the

environment under the influence of light and water. In a number of pest control preparations neopinamin=tetrametrin=tetralat is used. Photoresistant pyrethroid permetrin=corsaire is being investigated.

About 30% of the total amount of insecticides used to protect collections against pests consist of substances belonging to other groups of chemical compounds such as hydrogen cyanide, sodium arsenide, methylbromide, ethylene oxide, and boric acid. Selection depends upon physico-chemical properties of the preparation, the purpose and methods of its use, and cost. To protect collections, fumigants, aerosols, solutions, pesticide dusts and, less often, concentrates of emulsion and pastes are used.

Sensitivity of keratin-destroying beetles and moths to insecticides differs greatly with species and stage of development. Dermestid larvae and Tineida larvae show the greatest resistance. Dermestidae possess higher resistance to organophosphorus compounds than other insects. Insecticides of the same class of chemical compounds being used repeatedly over a long period increase the possibility of resistance.

To prevent this phenomenon it is recommended to use insecticides which belong to different classes of chemical compounds or alternate the chemical used.

Insecticides widely used in the USSR are: the fumigant methyl bromide, paradichlorobenzene, DDVP, lyndan, an aerosol which contains the active ingredient "Aeroantimol," neopinamin, boric acid dusts and soium arsenite in paste or solution.

Good results in pest control have been obtained by using iodphenphos , chlorpyriphos and pyriphos-methyl. However, for some reasons, the above compounds are not used in the USSR museums.

Prospective insecticides for pest control in museums are synthetic pyrethroids. At present, the possibility of using photoresistant pyrethroid - permetrin for the control of synanthropic insects is being comprehensively studied.

Five compounds were formerly used as fumigants for general disinfestation of depositories and use in chambers: carbon disulfide (CS_2), hydrogen cyanide, ethylene oxide, ethylenedichloride, carbon tetrachloride. At present they are not used for collections in our country, though abroad they are still used to protect museum exhibits against insects.[4] The chief reason for renouncing hydrogen cyanide is its extreme toxicity; carbon disulfide, ethylene oxide, ethylenedichloride (together with carbon tetrachloride) are hazardous because they are flammable and highly explosive. At present only methyl bromide is used.

Repellents are substances used to repel insects. Their application against insects is one of the most important preventative measures possible.

Not many repellents with well expressed action against moths and beetles of different species exist. Naphthalene, camphor, and paradichlorobenzene may be used as repellents against moths in collections. Study of behavioral responses of two dermestid species - Anthrenus picturatus and Attagenus smirnovi - to smells of camphor, naphthalene, lavender oil, paradichlorobenzene showed that the response of these beetles to smells is specific depending on species. Naphthalene reveals a weak repelling action on Att. smirnovi. Lavender oil proved to be a weak repellent against dermestid beetles of both species (less than 50% of specimens responded). Response of beetles to the smell of paradichlorobenzene was indifferent.[5] Thus, it is obvious that in museum depositories infected by several species of Dermestidae, application of camphor as repellent is insufficient, and application of naphthalene, lavender oil and pardichlorobenzene is useless.

Among synthetic repellents against blood-sucking insects there are a number of compounds which repel mass species of Dermestidae injurious to collections with good results. They are derivatives of hexamethylenimine (carboxide, oxamate); a group of amidoethers of carbon acids (benzimine); rebemide and DETA - of group diethylamids of carbon acids. Oxamate and rebemide proved to be active repellents for Anthrenus picturatus, and benzimine and DETA as well as carbozide actively repel Attagenus smirnovi.[6]

Antifeedants are those compounds which, when applied to a nutritive substrate, reduce or prevent entirely its being eaten by insects. It is essential to keep in mind that only complete treatment of the material protects it from being eaten by larvae of dermestid beetles and moths. In practice when protecting collections against insects, antifeedants may be used only for treating subsidiary materials, such as wrapping, interleaving, etc. Preparations containing Rebemide ("Suprosol," "Supromit") act as antifeedants on larvae of moths. Antifeedant action of the above mentioned preparation is weaker against the larvae of Dermestidae. An effective long-term antifeedant action against larvae of derestid pests is provided by carboxide.[7]

Attractants are substances which attract insects. As to the character of their

action, they are divided into two groups: sexual (attracting specimens of the opposite sex) and feeding.

Feeding attractants for moths and dermestid beetles are the following: the moths are attracted to the smell of fatty materials and sweat gland secretions, for beetles of Anthrenus Schaeff., Attagenus Latr. generas - the smell of flowers of some plants belonging to families Rosaceae and Umbelliferae.

Sexual attractants (pheromones) have been isolated and identified in a number of dermestid species. The possibility of using pheromone traps in the museum environment, when the quantity of insect pests is not large, is doubtful.

Specifications (both chemical and physical) of all the above-mentioned chemical compounds, including information as to their use and advice concerning storage, are given in detail in our Reference book.[8]

To ensure the safe keeping of collections it is necessary to carry out a whole complex of measures which, as regards their tasks and methods, may be divided as follows;
- preventative, aimed at preventing infestation by dermestid beetles and moths;
- curative, aimed at extermination of pests in collections.

Measures taken, curative or preventative, must be reliable and safe for collection materials and human beings.

<u>Preventive Inspection</u> a complex system of activity aimed at preventing infestation of collections by insects which includes both general and specific measures.

General preventative measures are aimed at preventing penetration of insects into museums, both from natural sources and from infected objects. One of the most important points in such a program is examination of returning exhibits as well as newly collected materials in a specially equipped chamber.

Specific preventive measures against dermestid beetles and moths take into consideration peculiarities of biology and physiology and require, in particular, the use of repellents and antifeedants specific to the species. For example, limiting or stopping the use of plants such as spiraea, mountain ash, hawthorn (Rose family), goutweed and chervil (Umbelliferae family) in areas adjoining the museum, because flowers of these plants attract dermestid beetles, thus helping them to accumulate in the immediate proximity of the museum. It is most expedient to carry out preventative treatment before the mass flight of synanthropic insects begins. The difficulty of eliminating infestations by insects (especially, by Dermestidae pests) makes preventive measures particularly important.[9]

Curative measures are used when it is positively ascertained that the collection is infested by insects. Both chemical and physical methods may be used for destroying them. Chemical methods are based on using insecticides. When collections are infested by dermestid beetles and moths, it is necessary to carry out both disinfestation of the premises, and of the materials in a fumigation chamber simultaneously. Only if both measures are carried out simultaneously will pest control be totally effective.

In the case of mass infestation by insect pests, best results are achieved with fumigation using methyl bromide. To treat museum materials a concentration of 25 g/m^3 for 72 hours must be used. Duration depends, in part, on the temperature at which the treatment is carried out. Dermestidae show strongest resistance to this gas at 0°C. The treatment is most effective at the temperature above 15°C. For fumigation of objects infested by moths the following temperature and conditions are advisable: 11-15°C - 300 hourgrams per cubic meter (product of average concentration by exposure time), at 16-20°C - 250 hourgrams per cubic meter, at 21-25°C - 200 hourgrams per cubic meter. As a whole, irrespective of the concentration of the fumigant, exposure must continue for not less than 4 hours.[3] It must be remembered that furs and other loose materials treated with methyl bromide retain traces of the gas for as long as a month. It is important to remember that methyl bromide and other fumigants have no residual protective action.

For disinfestation of collection materials it is convenient to use portable chambers using paradichlorobenzene as the fumigant.[10]

One of the most effective fumigants for disinfestation in confined spaces is DDVP (preparations "Molemor" and "Desmol").

For treatment of premises the author finds preparations based on "phosim" ("Aeroantimol"), of neopinamin ("Neopinat"), 55 water solution of chlorophos, most effective, and in a number of cases boric acid as a powder (when exposed for not less than 30 days) may be used.

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Working Group 26

Furniture

Meubles

SUMMARY

A number of ethical problems faced by furniture conservators are considered. Treatments carried out in the Furniture & Wooden Objects laboratory of the Canadian Conservation Institute are referred to as examples of specific problems.

THE FURNITURE AND WOODEN OBJECTS LABORATORY, THE CANADIAN CONSERVATION INSTITUTE: ITS PRACTICE AND PRINCIPLES

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Introduction

The Furniture & Wooden Objects laboratory currently consists of two conservators and one or more interns. Treatments are carried out on a large variety of historical wooden and composite artifacts ranging from small folk art sculpture to life-size vehicles and furniture from all historical periods with various types of finishes. The staff also provides training to interns in the laboratory and presents lectures and workshops to personnel of Canadian museums on the care and basic treatment of furniture collections. The CCI research scientists assist with specific problems such as paint analysis and conservators from other divisions provide advice if necessary, for the treatment of composite artifacts.

Practice

Treatment complexity varies from simple joint stabilization to major conservation. In the latter instance, because of the extremely damaged condition of an artifact, it may require more drastic treatment than would normally be carried out. Treatment may verge on restoration rather than conservation.

Fig. 1a: Before consolidation of painted surface and rush seating.

Fig. 1b: After treatment. Missing areas of rush weave were not replaced.

The treatment process is initiated by a proposal that is developed by the conservator based on the condition of the artifact and its use by the owning institution. The before- and after-treatment photographs of a small chair (Fig. 1a, b), illustrate the very minimal stabilization treatment that might be given to the painted surface of an artifact to be returned to storage, compared to the more extensive treatment given to the painted surface of an artifact that will be displayed in an historical house (Fig. 2a, b).

Once the treatment proposal is approved by the owning institution, extensive visual and written documentation is done. Occasionally some compromise is required in a treatment approach. The treatment requested for the rocking horse was to entirely inpaint the loss areas, an approach felt too drastic considering the extent of damage. The compromise reached was to lightly tone down the most visible areas of the ground using watercolors, so that within the room display the losses are quite indistinct. Although the rocking horse is not specifically furniture the same approach could apply to painted furniture.

In deciding the treatment of painted surfaces, the problem of the practicalities of consolidant reversibility arises. This is an ethical question faced by all conservators. The most suitable consolidant tested and the one used in treatment of the rocking

Fig. 2a: Before consolidation and toning down on loss area.

Fig. 2b: After treatment.

horse was dilute rabbitskin glue, and for the chair, a methyl cellulose in distilled water (2%). Both are reversible.

Fig. 3a: Encrustation on the surface before treatment.

Fig. 3b: After removal of the encrustation by the "drifting in" process.

Another consideration faced by furniture conservators is the approach to treating a deteriorated varnish finish. Treatment of a workable spirit varnish such as shellac in a solvent medium involves the process often referred to as "drifting in" whereby a wad slightly dampened with the solvent is drifted over the surface. Careful control of this technique can remove the top layer of grime and damage without disturbing lower layers. This approach was taken on a 19th century melodeon from an historical house (Fig. 3a, b). The shellac surface had been damaged during a fire. Tests showed that the white encrustation could be removed by the method described so that succeeding layers of the original finish remained intact. This method of treatment both stabilized the artifact and improved the appearance, enabling it to be displayed in the original room setting. However, it could be argued that even this minimal intervention is too severe since it does actually remove some top surface layers.

Treatment of a non-workable surface, such as a varnish which is often composed of synthetic resins and oils, and lacquers, is approached quite differently. The synthetic resin varnish surface of a 1940's ash desk to be displayed in a room setting was given minimal treatment. Although the surface was quite crazed, it was stable (Fig. 4a, b). The finish was wiped free of surface grime with a soft cloth moistened in mineral spirits. Loss areas were inpainted with tinted shellac in denatured alcohol after first sealing the bare surface with a brushing of blonde shellac. This inpainting can be reversed should more extensive treatment of the surface be preferred at some future date. Again, treatment stabilized the artifact, retained the original finish and achieved the display condition requested.

Experiments are taking place in the laboratory with various techniques to reproduce surface areas including silicone rubber impression molds of crazed patterns for loss replacement (1). The use of 1:1 photographs on archival quality materials to replace missing decorated or inlaid surfaces, a technique developed by Sheetz (2), is being adapted to replace loss areas on a sewing box surface which is intricately decorated with ivory, tin and wood pieces, the smallest of which measure 1-2 mm in diameter.

Treatment of gilded objects also requires ethical considerations. Traditionally, objects were often regilded, however, a more conservative approach is now being urged (3), and will be considered for two artifacts that recently arrived for treatment. One is a 19th century gilded side chair with major loss areas and unsuccessful previous restoration attempts, the other an 18th century English pier table that at some point had been stripped of its gilded surface and supporting layers. Treatment of the chair will probably consist of removing the previous infills which have separated, and infilling and regilding the loss areas only to match the existing original gilded surface. The owning institution has requested that the pier table be entirely regilded. It is most likely that this approach will be taken, as there is evidence that stripping of the original or most recent surface had been done by an antique dealer, and in its present condition the pier table is neither suitable for display nor a true example of a pier table of its period. Treatment that is actually restoration

Fig. 4a: Desk top before treatment. The light area of bare surface was inpainted.

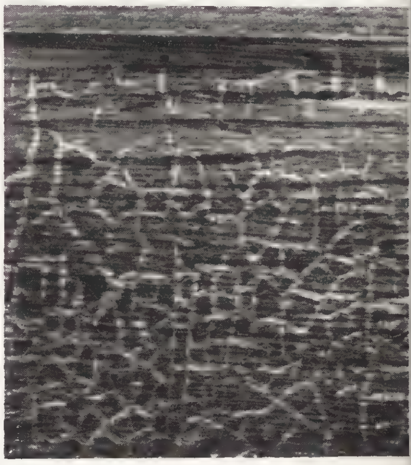

Fig. 4b: Detail of crazing. This stable finish was retained.

rather than conservation is felt justified in this instance.

Another important consideration in furniture conservation is the choice of adhesives. There are differing opinions among furniture conservators on the advantages and disadvantages of traditional glues which are reversible, sometimes too readily, over polyvinyl acetate emulsions and other modern synthetic adhesives. Some of these latter adhesives are either irreversible or theoretically reversible but in reality often cannot be reversed without further damage to the artifact. This problem is particularly relevant in Canada where many institution and private collections are housed in centrally heated environments where low humidity often causes the drying of animal glues and the release of joints and veneers. In the Furniture & Wooden Objects laboratory, animal glues are used in most treatments and occasionally, polyvinyl acetate emulsion. Choice of adhesive is based on the type of problem. Animal glue is always used for structural joins and veneers, while a polyvinyl acetate emulsion might be used for repair on an area that is not part of the original construction method of the artifact and therefore should not need to be reversed during any future treatment.

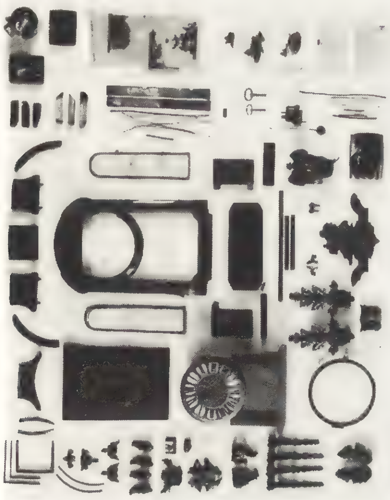

Fig. 5: The many sections of the structure, surface decoration and ormolu before treatment.

The most recent artifact received in the laboratory is an 18th century Boulle work bracket clock. It was acquired by the owning institution in a disassembled state and is considered an important acquisition (Fig. 5). There is evidence of previous restoration attempts. The final treatment decision will involve all of the considerations discussed above and others, such as the choice of replacement material for the extensive areas of inlay loss. Tortoiseshell is difficult to obtain in the quantity required and even if genuine shell can be obtained, should a readily identifiable synthetic material be used? A decision will have to be made whether to leave intact or replace the lesser quality inlay replacements done at an unknown point in the object's history.

Principles

When considering the extent of conservation treatment, furniture conservators, whether they are working on institution or private collections, are faced with a traditional expectation that furniture be maintained in perfect condition. Whereas a collector may accept the condition of an ethnographic or archaeological acquisition, such a condition often involving damaged or loss areas, this same collector acquiring a dining table with a slightly marked surface will probably have it restored to an unblemished appearance because the table will be utilized in a room setting. Should the home of this collector become an historical site at some later date, the governing institution is likely to request more drastic aesthetic conservation treatment of the furniture than would be expected in treating the ethnographic or archaeological artifacts displayed in the same setting. This may be due in part to the relatively recent development of furniture conservation as opposed to furniture restoration. While there are numerous publications available on restoration of furniture, the number of publications on conservation is minimal. Many conservators working in this discipline have a furniture design, construction or restoration background so their approach to a treatment may differ from that of a conservation programme graduate. This situation exists at the CCI and it certainly generates interesting debates on ethical considerations in the extent of treatments. Codes of Ethics already established in many conservation organizations provide general guidelines; however furniture conservators working within these parameters may be called upon to make compromises.

These problems are compounded by the relative isolation in which most furniture conservators work, the scarcity of training programmes for this discipline compared to those which address paintings conservation for example, (the CCI is the only Canadian institution providing furniture conservation training), and the lack of a major support group such as the ICOM Conservation Committee which has Working Groups for other disciplines.

Faced with the treatment of present and future collections of furniture constructed using modern techniques, and irreversible adhesives and finishes, furniture conservators will need to work together to overcome ethical and treatment problems.

It is hoped that formation of Working Group No. 26 Furniture will foster this type of communication.

Acknowledgement

The author wishes to thank the following institutions for permission to use documentation photographs of treatments carried out on objects from their collections:

Fig. 1, 2	The Prince Edward Island Museum and Heritage Foundation, Charlottetown,
Fig. 3	The Billings Estate Museum, Corporation of the City of Ottawa,
Fig. 4	History Division, Canadian Museum of Civilization, National Museums of Canada, Ottawa,
Fig. 5	Royal Ontario Museum, Toronto.

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RÉSUMÉ

Un cabinet en palissandre et en ébène, décoré de rinceaux d'ivoire et de pierres précieuses avec des colonnettes en cristal de roche a été conservé et sauvé de la dégradation causée par l'outrage des années. L'intérieur du cabinet qui est probablement espagnol est conçu comme la façade d'un palais maniériste. Les chapiteaux des colonnettes et les statuettes qui ornent la façade sont en bronze doré. Après un examen technique minutieux qui détermina les altérations, on fit une documentation précise et on commença les travaux de conservation. Après un démontage complet le meuble fut dépoussiéré et déciré avec précaution Les bronzes furent néttoyés et conservés. Le cristal de roche des colonnettes qui manquait a été reconstruit avec une résine polyester. Les pierres précieuses de l'incrustation qui avaient été perdues ont été substituées analogiquement. Les fragments de bois des entablements abimés ont été reconstruits. La finition fut réalisée avec une émulsion de cire diluée dans de l'essence avec du damara. Les conditions posées par les Monuments historiques furent témoigne d'une grande virtuosité professionnelle du conservateur qui a prolongé la vie de cette oeuvre.

CONSERVATION D'UN CABINET DU 17$^{\text{ième}}$ SIÈCLE

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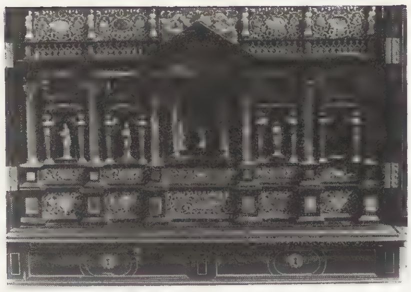
Le cabinet dont il est question est en bois de palissandre et d'ébène. Il est incrusté de filets d'ivoire disposés en filets géométriques et est posé sur un socle assez bas, muni de deux tiroirs. Ses pieds en bronze ont la forme de lions assis. Derrière la porte du cabinet, l'intérieur a été conçu comme la partie antérieure d'un palais. La façade est divisée par cinq niches entre des colonnettes tordues, en cristal de roche, dans lesquelles on a placé de petites statuettes de femmes en bronze doré et ciselé. Chaque niche est surmontée d'un fronton soit triangulaire, soit semi-circulaire porté par des espèces de pilastres à chapiteaux en forme de bustes. La niche centrale est plus grande et ses colonnettes portent sur un entablement une rangée de balustres, au-dessus desquelles on voit un pignon incrusté d'ivoire et de pierres. Les architraves posées sur le chapiteaux des colonnettes des niches à frontons sont garnies de rangées de balustres et de frises ornées de rinceaux d'ivoire et de pierres précieuses polies. Les pierres incrustées au centre des rectangles qui divisent la frise ont une forme ovale. Au-dessus de la grande niche, on a disposé sur les arêtes du pignon deux anges en bronze doré couchés. Les deux ailes de la porte extérieure sont décorées d'incrustations géométriques ainsi que l'envers du courvercle posé sur le dessus du cabinet. C'est sous ce couvercle qu'on a placé le médaillon d'ivoire avec les armoiries et le nom du 1er propriétaire du cabinet qui fut l'électeur de Mayence et évêque de Bamberg.[1]

La place du cabinet est de nos jours dans la salle de musique du château de Rájec en Moravie. C'est en 1861[2] qu'il avait été rénové pour la dernière fois. L'outrage des années devenait sensible et dégradait la valeur artistique de cette admirable oeuvre d'art. Il avait souffert au contact imprévu des doigts qui le touchaient. La poussière avait formé une croûte noire, notamment sur les détails en bronze doré. Les pierres précieuses étaient devenues ternes et un grand nombre d'entre elles manquaient. Certaines parties de l'incrustation d'ivoire s'étaient soulevées à la suite d'un pourcentage trop élevé d'humidité atmosphérique. Deux colonnettes en cristal de roche avaient été brisées mécaniquement et collées à l'aide d'une colle qui n'avait pas résisté à l'âge, ce qui les faisait gauchir. Des fragments du bois des corniches avaient été détachés ou rompus. En plus, le couvercle était bloqué faute de clés et les tiroirs visibles, ainsi que les tiroirs secrets se coinçaient et étaient difficiles à manoeuvrer.

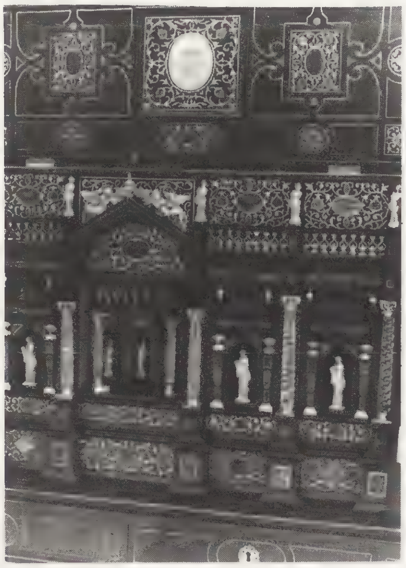
La responsable du mobilier du château de Rájec proposa la conservation du cabinet. Avec le consentement du Ministère de la Culture, le cabinet fut confié, en 1985, à un spécialiste[3] qui devait lui rendre son aspect d'origine, son intégrité esthétique et historique.

Le Processus de la Conservation

Après un examen technique minutieux qui détermina l'étendue des altérations, on fit la documentation et on procéda au démontage complet. Les serrures et les bronzes furent enlevés ainsi que les colonnettes en cristal de roche. Ensuite, on démonta - au nombre de 27 - tous les tiroirs du cabinet. Le meuble "ainsi déshabillé" fut dépoussiéré à fond et déciré avec de l'essence de térébenthine. Les serrures qu'on avait démontées furent nettoyées au pinceau trempé dans du pétrole. Les bronzes, c'est-à-dire les chapiteaux, les statuettes, les balustres, les plaques des serrures et les vises gravées qui étaient fortement oxydés et encrassés ont été baignés dans un produit chimique - chelaton 3 - et nettoyés avec une petite brosse. Après séchage, pour protéger la substance, on enduisit le dessus des pièces avec une laque transparente à base anti-acide. Les colonnettes de cristal de roche brisées et abimées par des fêlures ont été réparées avec une résine polyester et nettoyées avec de l'eau tiède où l'on avait fait dissoudre de la soude. Cette résine permit aussi de remodeler le fragment qui manquait à une des colonnettes. Pour coller le fragment, on a employé une colle spéciale pour verre fabriquée par les établissements Henkel. Les bouts des corniches qui manquaient ont été reconstruits en bois d'ébène et pour les fixer à leur place, on avait choisi la colle Araldit de Ciba qui s'était montrée très efficace. Les bandes en tôle qui fixaient les anses latérales du cabinet et qui étaient partiellement usées ont été remplacées par des copies. Pour substituer les 56 pierres de l'incrustation d'origine qui manquaient, il a fallu contacter un collectionneur et un tailleur de pierres précieuses. Pour trouver les agates jaunes, rouges, grises et les jaspes et les crevels dont les couleurs, la vivacité et le dessin correspondraient aux pierres restées en place et leur feraient pendant, on a dû surmonter beaucoup de difficultés. Lorsqu'on trouvait la pierre, il fallait la tailler, l'amincir (2 mm à 4 mm), lui donner la même forme et la polir. Pour fixer les pierres à leur place, on employait la colle Araldit. Les pierres qui étaient restées à leur place d'origine furent démontées, nettoyées mécaniquement et ravivées dans de l'acide oxalique. Pour remettre en place les quelques parties des rinceaux d'ivoire sortis de leur cannelure, il fallait les repousser avec une grande précaution et les



L'intérieur du cabinet conçu comme la façade d'un palais maniériste. (photo prise avant la conservation)



La partie centrale du cabinet après le redressement et la conservation des colonnettes en cristal de roche et la substitution des pierres précieuses qui manquaient.

coller avec grand soin. Simultanément, on a voulu nettoyer et conserver le médaillon votif en le frottant avec une émulsion à base de craie de Vienne et en le polissant à la cire. En excavant le médaillon, on a eu la surprise de trouver dans son lit ovale un feuillet nous informant de la rénovation au siècle passé.[4]

Il restait encore deux problèmes à résoudre: 1) les tiroirs qui étaient difficiles à ouvrir étaient tapissés à l'intérieur avec un papier décoré à la main et malgré sa détérioration, on hésitait à cause de son authenticité de le remplacer par un papier neuf. 2) le fond du cabinet, sur toute sa longueur, avait une large craquelure. Après avoir été enlevé avec précaution, le papier d'origine fut nettoyé mécaniquement. On enduisit le bois des tiroirs contre les moisissures avec un produit chimique nommé Luxol et on replaça le papier dans les tiroirs. Les lacunes furent complétées avec un papier neutre. Pour préparer le fond fendu du cabinet, on a collé un mince filet de bois dans la fêlure et toute la surface fut recouverte d'une laque noire. Après le remontage de tous les détails, on travailla à la finition. La surface extérieure de toutes les parties du cabinet fut enduite de cire d'abeilles diluée dans de l'essence avec un peu de damara. Le bois fut légèrement poli pour obtenir un aspect satiné.

Tous les travaux auxquels le cabinet avait été soumis ont été consultés avec une historienne d'art et chaque opération a été soigneusement documentée. Le résultat obtenu témoigne d'une grande virtuosité professionnelle du conservateur et de son respect pour le matériel historique. Il ne reste qu'à constater que les conditions posées et les exigences préliminaires des Monuments historiques ayant été respectées, une oeuvre d'art très précieuse a été sauvée de la dégradation et par la suite de son anéantissement.[5]

Légende

1. Sur les contours du médaillon on voit le relief de l'inscription votive: "VIVA. LOTHARL FRANCISCVS S. SEDIS MOGVNT. ECLECT. EPSICOPVS BAMBERGENSIS."

2. Le curriculum vitae du cabinet est presqu'entièrement plongé dans les ténèbres. Les artisans qui ont travaillé à sa réalisation sont anonymes. Ils n'ont laissé aucune trace de leur participation. Ce n'est que son style qui nous révèle son âge approximatif. Par contre, le maître artisan qui l'aura rénové à Vienne pour la famille Salm a laissé un témoignage évident de son travail en 1861.

3. La conversation a été confié au conservateur Miloslav Kubîk de Jablonec nad Nisou.

4. Sur le feuillet (2.5X8cm)m il est écrit en alphabet allemand: "Renoviert Johann Lip. (Z?) Wien 1 Jäner 1861 (bei G. Matyasofsky). Après l'avoir photographié, on a remis le document à sa place et on a ajouté un autre feuillet avec la date et la signature de la conservation actuelle.

5. Le cabinet conservé a été remis à sa place audit château d'Etat en 1985, au mois de novembre. Pour protéger la façade intérieure richement ornée du cabinet que l'on montre aux visiteurs, on a placé une plaque en "Plexiglas" devant sa face.

Appendix A

Directory Board/Conseil de Direction 1984–1987

Christian Lahanier
Chairman/Président
Laboratoire de Recherche des Musées de France
Palais du Louvre
75041 Paris Cedex 01
France
tel. 33 (1) 42.60.39.26
poste 34.47

Agnes Ballestrem
Vice Chairman/Vice Président
Central Research Laboratory for Objects of Art and Science
Postbox 5132
1007 AC Amsterdam
The Netherlands
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Eduardo Porta
Treasurer/Trésorier
Museo Arqueologico y Universidad de Barcelona
Parque de Montjuic
Barcelona 4
Spain
tel. 34 (3) 318.64.81

Steen Bjarnhof
Konservatorskolen
Esplanaden 34
1263 Copenhagen
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tel. 45 (1) 1268.60

Ivan Gorine
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1007 AC Amsterdam
The Netherlands
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Christoph von Imhoff
1 Place du Tilleul
1700 Fribourg
Switzerland
tel. 41 (37) 23.24.04

Hermann Kühn
Deutsches Museum
D-8000 München 22
Federal Republic of Germany
tel. 49 (89) 297.1273/1350

Susan Inman
Administrative Secretary/Secrétaire Administrative
ICCROM
Via di San Michele 13
00153 Rome
Italy
tel. 39 (6) 580.90.21

Cevat Erder
Ex-officio member/Membre ex-officio
Director, ICCROM
Via di San Michele, 13
00153 Rome
Italy
tel. 39 (6) 580.90.21

Norman Brommelle
Observer/Observateur
Secretary General, IIC
6 Buckingham Street
London WX2N 6BA
United Kingdom
tel. 44 (1) 839-5975

Brian V. Arthur
Coopted Member/Membre coopté
National Museum of Man
Ottawa, Ontario
Canada K1A 0M8
tel. 1 (819) 994-2354

Appendix B

Working Groups and Coordinators/Groupes de Travail et Coordonnateurs 1984–1987

1. Scientific Examination of Works of Art/Investigation scientifique des oeuvres d'art

Christian Lahanier
Laboratoire de Recherche des Musées de France
Palais du Louvre
F-75041 Paris Cedex 01
France
tel. 33 (1) 42.60.39.26, ext. 3445/3447

Pieter Meyers, Assistant Coordinator
Los Angeles County Museum of Art
Conservation Center
5905 Wilshire Boulevard
Los Angeles, CA 90036
U.S.A.
tel. 1 (213) 857-6010

Catheline Périer-d'Ieteren, Assistant Coordinator
Université Libre de Bruxelles
Faculté de Philosophie
50, avenue Franklin Roosevelt
CP 175
1050 Brussels
Belgium
tel. 32 (2) 649.00.30, ext. 3583/2419

2. Structural Restoration of Paintings on Canvas/Restauration structurale des peintures sur toile

Bent Hacke
Kunstmuseum, Faelleskonservering
Vennelystparken
8000 Arhus C.
Denmark
tel. 45 (6) 13.87.55

Gerry Hedley, Assistant Coordinator
Courtauld Institute
20 Portman Square
London W1H 0BE
United Kingdom
tel. 44 (1) 935-9292

3. Ethnographic Materials/Matériaux ethnographiques

Sue Walston
The Australian Museum
6–8 College Street
Sydney, N.S.W. 2000
Australia
tel. 61 (2) 339-8111

Richard R. Beauchamp, Assistant Coordinator
British Columbia Provincial Museum
675 Belleville Street
Victoria, B.C.
Canada V8W 1A1
tel. 1 (604) 387-3647

Puccio Speroni, Assistant Coordinator
Otto Monstedsgade 1
1571 Copenhagen V.
Denmark

4. Documentation/Documentation

Arlene Quint
2727 29th Street, N.W.
Washington, D.C. 20008
U.S.A.
tel. 1 (202) 332-5133

Janet Bridgland, Assistant Coordinator
The Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, CA 90292-6537
U.S.A.
tel. 1 (213) 822-2299

5. Polychromed sculpture/Sculpture polychrome

No program this trienniel period.
Aucun programme pour cette periode triennale.

6. Modern and Contemporary Art/Art moderne et contemporain

Paolo Cadorin
Picassoplatz 8
CH-4052 Basel
Switzerland
tel. 41 (61) 23.68.90

Daniele Giraudy, Assistant Coordinator
Musée Picasso
Château Grimaldi
F-06600 Antibes
France
tel. 33 (93) 33.67.67/34.17.89

Monique Veillon, Assistant Coordinator
Picassoplatz 8
CH-4052 Basel
Switzerland
tel. 41 (61) 23.68.90

7. Wet Organic Archaeological Materials/Matériaux organiques archéologiques gorgés d'eau

David Grattan
Canadian Conservation Institute
1030 Innes Road
Ottawa, Ontario
Canada K1A 0M8
tel. 1 (613) 998-3721

Per Hoffman, Assistant Coordinator
Deutsches Schiffahrtsmuseum
Van-Ronzelen-Strasse
D-2850 Bremerhaven
Federal Republic of Germany

8. Reference Materials/Materiaux de référence

Lambertus Van Zelst
Conservation Analytical Laboratory
Office MSC
Smithsonian Institution
Washington, D.C. 20560
U.S.A.
tel. 1 (202) 287-3700

Jacob Mosk, Assistant Coordinator
Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap
Postbox 5132
1007 AC Amsterdam
The Netherlands
tel. 31 (20) 737 911/735 162

9. Textiles/Textiles

Judith Hofenk de Graaff
Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap
Postbox 5132
1007 AC Amsterdam
The Netherlands
tel. 31 (20) 737911/735162

Mechthild Flury-Lemberg, Assistant Coordinator
Abegg-Stiftung Bern
CH-3132 Riggisberg
Switzerland

10. Stone/Matériaux pierreux

Josef Riederer
Staatliche Museen Preussischer Kulturbesitz
Rathgen-Forschungslabor
D 1000 Berlin 30
Federal Republic of Germany
tel. 49 (30) 320.1297

Elena Charola, Assistant Coordinator
c/o ANDESUD
Avenida Puente Roque Saenz Peña 811 7°c
1035 Buenos Aires
Argentina
tel. 54 (1) 45-9693

11. Theory and History of Restoration/Théorie et histoire de la restauration

Ernst Van de Wetering
Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap
Postbox 5132
1007 AC Amsterdam
The Netherlands
tel. 31 (20) 735162

Hermann Kühn, Assistant Coordinator
Deutsches Museum
D-8000 München 22
Federal Republic of Germany
tel. 49 (89) 297.1273/1350

12. Care of Works of Art in Transit/Protection des oeuvres d'art pendant le transport

Sarah Staniforth
The National Trust
36 Queen Anne's Gate
London SW1H 9AS
United Kingdom
tel. 44 (1) 222-9251

Peter Wilson, Assistant Coordinator
Department of Exhibitions and Technical Services
The Tate Gallery
Millbank
London SW1P 4RG
United Kingdom
tel. 44 (1) 821-1313

13. Natural History Collections/Collections d'histoire naturelle

Frank Howie
British Museum (Natural History)
Cromwell Road
London SW7 5BD
United Kingdom
tel. 44 (1) 589-6323, ext. 740

Velson C. Horie, Assistant Coordinator
Manchester Museum
The University
Manchester M13 9PL
United Kingdom

14. Graphic and Photographic Documents/Documents graphiques et photographiques

Françoise Flieder
Centre de Recherches sur la Conservation des Documents Graphiques
Muséum National d'Histoire Naturelle
36, rue Geoffroy-Saint-Hilaire
F-75005 Paris
France
tel. 33 (1) 45.87.06.12

Klaus Hendriks, Assistant Coordinator
Picture Conservation Division
Public Archives of Canada
395 Wellington Street
Ottawa, Ontario
Canada K1A 0N3
tel. 1 (613) 996-1573

15. Mural Paintings and Mosaics/Peintures murales et mosaïques

Marcel Stefanaggi
Laboratoire de Recherche des Monuments Historiques
Château de Champs-sur-Marne
F-77420 Champs-sur-Marne
France
tel. 33 (6) 005.01.45

Eudald Guillamet, Assistant Coordinator
Patrimoni Artistic Nacional
Casa de la Vall
Principat d'Andorra
1040 Brussels
Belgium
tel. 33 (78) 21234/24077

16. Resins: Characterization and Evaluation/Résines: Caractérisation et évaluation

Eddy de Witte
Institut Royal du Patrimoine Artistique
1 Parc du Cinquantenaire
1040 Brussels
Belgium
tel. 32 (2) 735.41.60

Norman Tennent, Assistant Coordinator
Glasgow Museums and Art Galleries
Kelvingrove
Glasgow G3 8AG
United Kingdom
tel. 44 (41) 357-3929

17. Lighting and Climate Control/Eclairage et contrôle du climat

Gaël de Guichen
ICCROM
13 Via di San Michele
00153 Rome
Italy
tel. 39 (6) 589.26.22/ou 580.90.21

Brian Ramer, Assistant Coordinator
20-22 Torpichen Street
Edinburg, Scotland
United Kingdom

18. Conservation of Leathercraft and Related Objects/Conservation des cuirs artisanaux et objets similaires

Todor Stambolov
Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap
Postbox 5132
1007 AC Amsterdam
The Netherlands
tel. 31 (20) 737911/735162

Monique Berends-Albert, Assistant Coordinator
Dellaertlaan 15
1171 HE Badhoevedorp
The Netherlands

19. Easel Paintings on Rigid Support
Peintures de chevalet sur supports rigides

Christoph von Imhoff
Place de Tilleul, 1
CH-1700 Fribourg
Switzerland
tel. 41 (37) 23.24.04

Gerry Hedley, Assistant Coordinator
Courtauld Institute
20 Portman Square
London W1H 0BE
United Kingdom
tel. 44 (1) 935-9292

20. Glass, Ceramics and Related Materials/Verres, céramiques et matériaux apparentés

Norman Tennent
Glasgow Museums and Art Galleries
Kelvingrove
Glasgow G38AG
United Kingdom
tel. 44 (41) 357-3929

Carol Aiken, Assistant Coordinator
c/o Brian Ramer
20–22 Torpichen Street
Edinburgh, Scotland
United Kingdom

21. Training in Conservation and Restoration/Formation en conservation et restauration

Colin Pearson
Conservation of Cultural Materials
Canberra College of Advanced Education
P.O. Box 1
Belconnen ACT 2616
Australia
tel. 61 (62) 522111/522368

Barbara Roberts, Assistant Coordinator
The J. Paul Getty Museum
P.O. Box 2112
Santa Monica, CA 90406
U.S.A.
tel. 1 (213) 459-7611, ext. 240

22. Metals/Métaux

Cliff McCawley
Canadian Conservation Institute
1030 Innes Road
Ottawa, Ontario
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tel. 1 (613) 998-3721

David A. Scott, Assistant Coordinator
Department of Conservation and Materials Science
Institute of Archaeology
31–34 Gordon Square
London WC1H 0PY
United Kingdom
tel. 44 (1) 387-9651

23. Icons/Icônes

Ivan P. Gorine
VNIIR
10 Khrestyanskaya pl.
Moscow
USSR
tel. 7 (095) 271.28.68

Olga Lélékova, Assistant Coordinator
Institut de Recherches Scientifiques de l'URSS pour la Restauration
VNIIR
10 Khrestyanskaya pl.
Moscow
USSR
tel. 7 (095) 271.28.68

24. Rock Art/Art rupestre

Eduardo Porta
Museo Arqueólogico y Universidad de Barcelona
Parque de Montjuic
Barcelona 4
Spain
tel. 34 (3) 318.64.81

Ian Wainwright, Assistant Coordinator
Canadian Conservation Institute
1030 Innes Road
Ottawa, Ontario
Canada K1A 0M8
tel. 1 (613) 998-3721

25. Control of Biodeterioration/Contrôle de la biodétérioration

Fred Greene
Glenbow Museum
9th Avenue and 1st Street SE
Calgary, Alberta
Canada T2G 0P3
tel. 1 (403) 264-8300

Antonia Bakkenist, Assistant Coordinator
Durgerdammerdijk 123
1026 CG Amsterdam
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tel. 31 (2904) 300

Alan Postlethwaite, Assistant Coordinator
Conservation Analytical Laboratory
Office MSC
Smithsonian Institution
Washington, D.C. 20560
U.S.A.
tel. 1 (202) 287-3700

26. Furniture/Meubles

Anna Østrup
7, rue Visconti
F-75006 Paris
France
tel. 33 (1) 43.54.52.62

Appendix C

ICOM Committee for Conservation

Composition and working rules

1. The Committee and its aims

1.1 *The ICOM Committee for Conservation* is a permanent committee of the International Council of Museums.

Among its aims are:

a. The achievement and maintenance of the highest standards of conservation and examination of historic works by bringing together from all countries those who are responsible for cultural property: restorers, research workers and curators.

b. to promote research of a scientific or technological nature pertaining thereto.

c. to collect data and information about materials and workshop methods.

d. to make generally available by publication or otherwise the results of such enquiries.

1.2 The ICOM Committee for Conservation is composed of the Directory Board, Working Groups with their Coordinators, members of ICOM in good standing who have selected the Conservation Committee as the sole International Committee on which to vote in accordance with Article 31 of ICOM statutes, and coopted members, as provided in Articles 11 and 15 of the Rules and Procedures for the International Specialized Bodies of ICOM. The members of the Directory Board and the Coordinators must be members of ICOM or must undertake to become members within three months of appointment.

2. Directory Board

2.1 The Directory Board (hereinafter called the Board) is composed of eight members elected for three years by the Committee and one ex-officio member, namely the Director of ICCROM. Members are eligible for reelection.

2.2 The Board elects its Chairman from among the elected members and appoints an Administrative Secretary and a Secretary for Publications.

2.3 Among the elected members of the Board, who may also be Coordinators, should be represented Museum Curators, Restorers and Museum Scientists.

2.4 Delegates from international organizations such as UNESCO, IIC, and ICOMOS will normally be invited to attend meetings of the Board as observers.

2.5 The Board will endeavour to meet at least once every year.

2.6 The functions of the Board are the following:

a. to appoint Coordinators for definite tasks and for fixed periods of time.

b. to establish with Coordinators the programme of the Committee for Conservation.

c. to control the progress of work.

3. Coordinators

3.1 Coordinators will hold their offices at the discretion of the Board.

3.2 The Coordinator will choose the members of his Working Group in consultation with and with the approval of the Board and will direct its activities.

Statuts

1. Le comité es ses buts

1.1 *Le Comité de l'ICOM pour la Conservation* est un comité permanent du Conseil International des Musées.

Ses buts sont entre autres:

a. d'atteindre et de maintenir le plus haut niveau de la conservation et de l'examen des oeuvres d'art en mettant en contact ceux qui—dans tous les pays—sont responsables pour les biens culturels: restaurateurs, chercheurs scientifiques et conservateurs.

b. de promouvoir des études scientifiques ou technologiques relatives à cet objectif.

c. de réunir des données et des informations sur les matériaux et les méthodes d'atelier.

d. de diffuser les résultats de telles enquêtes par des publications ou autrement.

1.2 Le Comité de l'ICOM pour la Conservation est composé d'un Conseil de Direction, de Groupes de Travail avec leurs Coordinateurs, de membres d l'ICOM dont la situation est en règle et qui ont choisi le Comité pour la Conservation comme seul Comité International dans lequel ils ont le droit de vote suivant l'article 31 des Statuts de l'ICOM ainsi que de membres cooptés comme le prévoient les articles 11 et 15 du Règlement des Organes internationaux spécialisés. Les membres du Conseil de Direction et les Coordinateurs doivent être membres de l'ICOM ou le devenir dans les trois mois qui suivent leur nomination.

2. Le Conseil de Direction

2.1 Le Conseil de Direction (appelé le Conseil ci-dessous) est composé de huit membres élus pour trois ans par le Comité et du Directeur de l'ICCROM, qui en fait partie ex officio. Les membres peuvent être réélus.

2.2 Le Conseil choisit son Président parmi les membres élus et nomme un Secrétaire Administratif et un Secrétaire aux Publications.

2.3 Parmi les membres élus du Conseil, qui peuvent être également des Coordinateurs, les conservateurs de musée, les restaurateurs et les spécialistes de laboratoire de musée doivent être représentés.

2.4 Des représentants des organisations internationales comme l'UNESCO, l'IIC et l'ICOMOS seront généralement invités à assister aux réunions du Conseil à titre d'observateur.

2.5 Le Conseil essayera de se réunir au moins une fois par an.

2.6 Les fonctions du Conseil sont les suivantes:

a. de nommer les Coordinateurs pour des tâches bien déterminées et pour des périodes fixées.

b. d'établir le programme du Comité pour la Conservation en accord avec les Coordinateurs.

c. de contrôler le progrès des travaux.

3. Coordinateurs

3.1 Les Coordinateurs garderont leurs fonctions sous l'approbation du Conseil.

3.2 Le Coordinateur choisit les membres de son Groupe de Travail en consultation et avec l'approbation du Conseil et en dirige les activités.

3.3 With the approval of the Board the Coordinator may organize joint meetings of specialists in his field, visits to laboratories, sites etc., having a direct bearing on the progress of his investigation.

3.4 Each Coordinator will submit, annually, to the Secretariat of the Committee for Conservation and not later than three weeks before the meeting of the Board, a report on the progress of the work of his group.

4. Working Group Members

4.1 On a proposal from the Coordinator, and with the approval of the Board, members will be assimilated in a group and be allocated a particular subject to study.

5. Procedure and Finance

5.1 The Committee for Conservation meets normally every three years in full session to hear reports on the progress of the work being carried out by the Working Groups under their Coordinator, to propose future programmes to the Board, and to encourage contact between the members of the Working Groups.
All interested persons may attend meetings with the approval of the Chairman of the Board.

5.2 While Groups meet by arrangement at times found to be most expedient, the Board will endeavor to meet annually.

5.3 Manuscripts prepared by Working Groups which are ready for publication shall be passed to the Secretary for Publications for submission to the International Coordination Committee for Publications.

5.4 The Committee's budget will be submitted for approval every three years to the full session of the Committee.

6. Amendments

The Board will have the power to make provisional changes in the composition and working rules to be presented for ratification at the next meeting of the Committee.

3.3 Le Coordinateur peut organiser avec l'agrément du Conseil des réunions de specialistes dans la matière de son ressort, des visites aux laboratoires, sites, etc. directement liées au progrès de son travail.

3.4 Chaque année et trois semaines avant la réunion du Conseil au plus tard le Coordinateur envoie au Secrétariat du Comité pour la Conservation un rapport sur l'état d'advancement du travail de son groupe.

4. Les membres des Groupes de Travail

4.1 Sur la proposition du Coordinateur et avec l'approbation du Conseil, des membres seront assimilés dans un groupe pour l'étude d'un sujet déterminé.

5. Fonctionnement et Finances

5.1 Le Comité pour la Conservation se réunit normalement tous les trois ans en séance plénière pour entendre les rapports sur l'avancement des travaux exécutés par les Groupes de Travail sous la direction du Coordinateur, afin de proposer les programmes futurs au Conseil et d'encourager les contacts entre les membres des Groupes de Travail.
Toutes les personnes intéressées peuvent assister aux réunions du Comité avec la permission du Président du Conseil.

5.2 Les Groupes de Travail arrangent des réunions aux moments les plus propices; le Conseil tâchera de se réunir chaque année.

5.3 Les manuscrits préparés par les Groupes de Travail destinés à être publiés seront envoyés au Secrétaire aux Publications afin d'être soumis au Comité International de Coordination pour les Publications.

5.4 Tous les trois ans le budget du Comité est soumis à l'approbation du Comité en séance plenière.

6. Amendements

Le Conseil peut faire des changements provisoires dans les Statuts à presenter pour une ratification à la prochaine réunion du Comité.

By-laws for the Election of the Directory Board

1. The election of the Directory Board by the Committee takes place every three years during the Plenary Meeting of the Committee.
2. The Directory Board is elected by those members of the Committee who are present at the Plenary Meeting.
3. All electors are eligible.
4. Members can put themselves up for election by informing the Secretariat either orally or in writing of their candidacy not later than 24 hours before the election. No candidates can be accepted after this deadline. Candidates should mention to the Secretariat whether they consider themselves a curator, restorer or scientist.
5. It is not necessary for a candidate to support his candidacy with signatures of members. A provisional list of candidates containing at least sixteen names in alphabetical order is prepared by the Directory Board.
6. The Secretariat prepares a voting-ballot by arranging the candidates in three columns according to their belonging to one of the three categories: curators, restorers or scientists. Each candidate can appear in only one column. Initials and full name of the candidate should be mentioned on the voting-ballot.

Règlement pour les élections du Conseil de direction

1. L'élection du Bureau directeur par le Comité prend place chaque trois ans durant la Réunion plénière du Comité.
2. Le Conseil de Direction est élu par les membres du Comité présents à la Réunion plénière.
3. Tous les électeurs sont éligibles.
4. Les membres peuvent se présenter eux-mêmes aux élections en informant le Secrétariat, soit oralement soit par écrit, de leur candidature pas plus tard que 24 h avant l'élection. Aucun candidat ne peut être accepté après cette date limite. Les candidats mentionneront au Secrétariat qu'ils sont conservateur, restaurateur ou chercheur.
5. Il n'est pas nécessaire pour un candidat de faire appuyer sa candidature par des signatures de membres. Une liste provisoire des candidats comprenant au moins seize noms dans l'ordre alphabétique est préparée par le Comité directeur.
6. Le Secrétariat prépare les bulletins de vote en répartissant les candidats en trois colonnes suivant qu'ils appartiennent à l'une des trois catégories: conservateur, restaurateur ou chercheur. Chaque candidat ne peut apparaître que dans une seule colonne. Les initiales et le nom entier du candidat seront mentionnés sur le bulletin de vote.

7. Prior to the election the Secretariat shall distribute one voting-ballot only to each individual member. The Secretariat shall keep a record of this distribution.

8. Prior to the election a Supervisor of the election is appointed from among the members present as well as two Overseers. The Supervisor opens the voting-boxes and reads the results. These are recorded by two persons appointed by the Secretariat. The Overseers check that the votes are correctly recorded.

9. Each member shall name a maximum of eight and a minimum of six candidates on the voting-ballot by placing a cross behind their names. Each column, corresponding with a category of curators, restorers or scientists should contain at least two crosses. Voting-ballots containing more than eight and less than six crosses are void.

10. Members shall put their individual voting-ballot into a previously sealed voting-box. Voting-ballots should be signed by the Supervisor before being put into the voting-box.
Voting-ballots not carrying the signature or initials of the Supervisor are void.

11. When the time allotted for the voting is expired the voting-boxes shall be assembled and opened by the Supervisor whereupon the public counting of the votes shall proceed.

12. The number of crosses appearing after the names of a candidate is recorded. When all voting-ballots have thus been counted the numbers are added up.

13. First elected are the two candidates in each column who have acquired the greatest number of votes. When two candidates in one category have obtained an equal number of votes and this number is greater than that of any other candidate in that category, they shall both be elected. When three or more candidates in one category have the same number of votes and this number is greater than that of any other candidate in that category two of them shall be assigned by lot. When two or more candidates in one category have acquired an equal number of votes and this number is smaller than that obtained by one other candidate in that category but greater than that acquired by any other candidate in that category one of these candidates shall be assigned by lot.

14. When thus the first six members of the Directory Board have been elected two further members shall be elected from among the remaining candidates, i.e., the two remaining candidates from any category having acquired the greatest number of votes. When two of the remaining candidates have obtained the same number of votes greater than that of any other remaining candidate they shall both be elected. When three or more of the remaining candidates have obtained the same number of votes and this number is greater than that of the other remaining candidates two of them shall be assigned by lot. When the above situations do not occur and two or more remaining candidates have acquired the same number of votes and this number is smaller than that obtained by one other remaining candidate but greater than that obtained by all other remaining candidates, one of them shall be assigned by lot. Assigning by lot is carried out by the Supervisor according to a procedure of his choice. When more than two candidates from the same country are elected only the two candidates having acquired the greatest number of votes or being assigned by the above described procedure are confirmed. The vacancy thus created shall be filled by applying the procedure described in articles 13 and 14.

7. Avant l'élection le Secrétariat distribuera un bulletin de vote à chaque membre individuel. Le Secrétariat tiendra un registre de cette distribution.

8. Avant l'élection un Président de l'élection est nommé par les membres présents ainsi que deux Assistants. Le Président ouvre les urnes et lit les résultats. Ils sont enregistrés par deux personnes nommées par le Secrétariat. Les Assistants contrôlent que les votes sont correctement enregistrés.

9. Chaque membre pourra nommer un maximum de huit et un minimum de six candidats sur le bulletin de vote en plaçant une croix derrière leurs noms. Chaque colonne correspondant à une catégorie de conservateurs, restaurateurs ou chercheurs contiendra pour le moins deux croix. Les bulletins contenant plus de huit et moins de six croix sont nuls.

10. Les membres devront mettre leur bulletin de vote individuel dans une urne scellée auparavant. Les bulletins de vote seront signés par le Président avant d'être mis dans l'urne.
Les bulletins de vote ne portant ni la signature ni les initiales du Président sont nuls.

11. Le temps alloué au vote terminé, les urnes seront rassemblées et ouvertes par le Président; ensuite les votes seront comptés en public.

12. Le nombre des croix apparaissant après le nom d'un candidat est enregistré. Quand tous les bulletins de vote ont été comptés, les nombres sont additionnés.

13. Sont élus en premier les deux candidats qui, dans chaque colonne, ont acquis le plus grand nombre de votes. Quand deux candidats d'une même catégorie ont obtenu un nombre égal de votes et ce nombre est plus grand que celui de quelque autre candidat dans cette catégorie, ils seront considérés comme élus ensemble. Quand trois candidats ou plus dans une même catégorie ont le même nombre de votes et que ce nombre est plus grand que celui de quelque autre candidat dans cette catégorie, deux d'entre eux seront tirés au sort. Quand deux ou plusieurs candidats dans une même catégorie ont acquis un nombre égal de votes et que ce nombre est plus petit que celui obtenu par un autre candidat dans cette catégorie, mais plus grand que celui acquis par un autre candidat dans cette catégorie, un de ces candidats sera tiré au sort.

14. Ainsi quand les six premiers membres du Bureau directeur ont été élus deux autres membres seront élus parmi les candidats restants, c.à.d. les deux candidats restants de quelque catégorie ayant acquis le plus grand nombre de votes. Quand deux des candidats restants ont obtenu le même nombre de votes plus grand que celui d'un autre candidat restant, ils seront élus. Quand trois ou plus des candidats restants ont obtenu le même nombre de votes et que ce nombre est plus grand que celui des autres candidats restants, deux d'entre éux seront tirés au sort. Quand les deux situations mentionnées ci-dessus ne se produisent pas et deux ou plus des candidats restants ont obtenu le même nombre de votes et que ce nombre est plus petit que celui obtenu par un autre candidat restant mais plus grand que celui obtenu par tous les autres candidats restants, un d'entre eux sera tiré au sort. Le tirage au sort est mis à exécution par le Président suivant une procédure de son choix. Si plus de deux candidats sont élus d'un seul pays, seuls les deux candidats ayant obtenu le plus grand nombre de votes ou étant assignés par la procédure décrite ci-dessus seront confirmés. Le vide créé ainsi sera rempli par l'application des articles 13 et 14.

15. The newly elected Directory Board assumes its functions from the moment that the results are read to the Plenary Meeting by the Supervisor or the Secretariat.

16. The Supervisor shall decide in matters arising during the electoral procedure for which these By-Laws do not provide.

17. Immediately after the election of the Board, a Chairman and Vice-chairman will be elected. To this purpose the previous Secretary will provide appropriate ballots and conduct the election. The person acquiring the largest number of votes will be elected Chairman and the person receiving the next largest number will be Vice-chairman. In case of a tie for either office a second round of voting will take place between the candidates who have tied.
In accordance with article 13 of the Rules of Procedure for the International specialized bodies of ICOM no Chairman or member of the Board may remain in office for a period exceeding six consecutive years.

18. As soon as possible, following the election of the Chairman and Vice-chairman, the Secretary of the Committee shall be appointed by the Board.

15. Les nouveaux élus du Bureau directeur assument leurs fonctions à partir du moment où les résultats sont lus à la Réunion plénière par le Président ou le Secrétariat.

16. Le Président décidera en la matière survenant durant la procédure électorale pour laquelle ces lois n'auraient rien prévu.

17. Immédiatement après l'élection du Conseil de direction un président et un vice-président seront élus. A cette fin l'ancien secrétaire qui est responsable de tout ce qui se rattache à l'élection, distribuera des bulletins de vote appropriés. La personne ayant reçu le plus grand nombre de votes sera élu président et la personne suivante sera vice-président. Dans le cas d'un même nombre de votes pour ces deux fonctions il y aura un second tour scrutin entre les candidats ayant reçu le même nombre de votes.
Conformément à l'article 13 du Règlement des organes internationaux spécialisés de l'ICOM le Président et les membres du Conseil de direction ne peuvent rester en fonction plus de six ans de suite.

18. Le plus tôt possible après l'élection du président et du vice-président, le Conseil désignera le nouveau secrétaire du Comité.

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ICOM COMMITTEE FOR CONSERVATION

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COMITÉ DE L'ICOM POUR LA CONSERVATION